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STUDY OF DUCTILE COATINGS FOR THE OXIDATION PROTECTION OF COLUMBIUM AND MOLYBDENUM ALLOYS

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Final Report

Covering period 1 July 1963 through 30 June 1964

PREPARED UNDER BUREAU OF NAVAL WEAPONS CONTRACT NOw 63-0706-c

By J. J. Burbank and F. H. Girard

METALS & CONTROLS INC.
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TEXAS INSTRUMENTS
INCORPORATED

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By J. J. Buchinski and E. H. Girard

METALS & CONTROLS INC.
Attleboro, Massachusetts, U.S.A.
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ABSTRACT

Platinum and Pt-10% Rh were examined as potential ductile oxidation resistant coatings for FS-85 (Cb-28Ta-10W-1Zr) and TZM (Mo-0.5Ti-0.1Zr). Oxidation tests on coating materials showed that 2-mil thicknesses would provide over 100 hours of protection up to 3000°F in the absence of diffusion degradation.

Roll bonded and hermetically sealed binary composites were evaluated for oxidation and diffusion behavior. Coating lifetimes of 5 to 15 hours at 2550°F were attained before diffusion induced failure occurred. No significant differences were observed between static and cyclic oxidation behavior. Failure mechanisms of FS-85 and TZM composites were shown to be substantially different from each other.

Six materials were evaluated in screening tests for potential diffusion barriers. Only ZrO_2 showed any merit, while Re, Au, Al, BN and Al_2O_3 did not.

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I. INTRODUCTION

Increases in the efficiencies of engines, and the construction of re-usable space vehicles, must necessarily be preceded by the development of structural components which can withstand high temperature oxidizing environments.

In view of this, the refractory metals and their alloys have received considerable attention. Many of them are capable of providing the necessary high temperature strength, but lack sufficient oxidation resistance. For this reason a large effort, involving numerous organizations, has been directed towards the development of oxidation-resistant coatings.

Silicides, aluminides, and their modifications have been used with some degree of success in coatings. These are relatively brittle substances, however, and their protective lives are seriously reduced when subjected to thermal or mechanical fatigue, or to shock loading. Their shortcomings are magnified with increasing temperature, limiting the number of situations in which they may be used effectively, as well as imposing serious restrictions on the design of hardware calling for their use.

This program was initiated to explore ductile coating materials which might, as a consequence of their ductilities, be superior to previously developed coating. Specifically, a coating was sought which would be ductile, or at least flexible, and which would provide 100 hours of protection to columbium and molybdenum alloy sheet at temperatures up to 3000°F without degrading the substrate.

One molybdenum and one columbium alloy were selected for the investigation. They were, respectively, TZM (Mo-.5Ti-.1Zr) and FS-85 (Cb-28Ta-10W-Zr). These alloys were considered to be two of the more promising refractory metal alloys and were recommended for further development by the Refractory Metal Sheet Rolling Panel of the Materials Advisory Board (Ref. 1).

Platinum and platinum-rhodium alloys were initially suggested as the most logical coating materials. This suggestion was confirmed in an extensive literature search, which led to the selection of pure platinum and the platinum-10% rhodium alloy as coating materials for investigation in this program. Past work has indicated the necessity for the development of a diffusion barrier between these coatings and the selected base metals to prevent diffusion which would lead to degradation of the composites.

The first step in the program consisted of a thorough literature search to obtain up-to-date data on platinum and its alloys (principally oxidation data), coatings in general (including compositions, preparation techniques, test procedures, and test results), platinum coatings in particular and on diffusion barrier materials. Most of the literature pertinent to this program is referenced in this report and has been annotated in the bibliography.

On the basis of the literature search the program developed three major areas of experimental investigation:

1. Coating Material Oxidation

    a. Base line data for use in judging the results of tests on coating-base metal composites.

    b. Data indicating the extent to which variations in test conditions - air flow, specimen position, and humidity - might affect the oxidation rate.

2. Coating-base Metal Composites

    a. Development of preparation techniques for test samples.

    b. Development of oxidation test procedures.

    c. Investigation of the diffusion mechanism leading to coating failure.

        (1) Metallographic examinations of diffusion.

        (2) Microhardness traverses through zones of diffusion.

        (3) Electron beam microprobe traverses through zones of diffusion.

3. Diffusion Barriers

    a. Development of preparation techniques for test samples.

    b. Diffusion "screening" tests.

    c. Evaluation (primarily metallographic).

A discussion of the materials selected and the results of the work in the three areas of investigation outlined above are presented in the following sections.

II. MATERIALS

A. Substrate Materials

As has been previously indicated, the molybdenum and columbium alloys selected for this investigation were, respectively, TZM (Mo-.5Ti-.1Zr) and FS-85 (Cb-28Ta-10W-1Zr). They were purchased from Fansteel Metallurgical Corporation in the form of sheet approximately 60 mils thick. Results of receiving inspection showed all of the materials to be within accepted specifications and generally of good quality. Certified chemical analyses were obtained for each alloy and are presented in Table I.

In sheet form the FS-85 alloy was easily given over 75% reduction in rolling with no apparent ill effects. As expected, however, it was necessary to "warm roll" the TZM alloy to avoid cracking.

The effect of high temperature oxidation on these two alloys differs greatly, as the oxides formed from TZM are predominantly volatile, while the oxides from the FS-85 are not.

B. Coating Materials

Of the metals and alloys presently available, only platinum and platinum-rhodium alloys with 40% or less rhodium have the necessary oxidation resistance, ductility and melting point to meet the coating objectives of this program.

It is perhaps interesting to note that only gold or rhodium may be added to platinum without reducing its oxidation resistance. Platinum-gold alloys have been ignored because of the decrease in refractoriness produced by gold additions, and the platinum-rhodium alloys containing greater than 40% rhodium have been ignored because they are lacking in ductility.

Two coating materials were selected for these studies: (1) platinum, and (2) its 10% rhodium alloy (to represent the ductile platinum-rhodium alloy group).

Analyses of the coating materials used in the studies discussed in this report are given in Tables II, III, and IV.

In one instance the platinum received was found to contain a rather significant amount of palladium, about 2.5%, as indicated in Table III. The scarcity of platinum at the time would have necessitated a test delay of several weeks before receipt of pure platinum replacement material. Normally such a wait would not have been necessary; however, platinum had recently become more difficult to acquire on the open or "free" market. Its scarcity has primarily been due to the unavailability of Russian platinum, since her

current internal consumption for new chemical plants has adsorbed such large quantities. South African production increases and the expected return of Russian platinum to the free market should shortly relieve the situation (Ref. 2).

In view of the possible delay, the probability of obtaining useful results from the platinum-palladium alloy was given considerable attention and the alloy was eventually used in a study. It will be discussed further in a later section of this report.

C. Diffusion Barrier Materials

Seven materials were selected as potential diffusion barrier formers:

(1) Rhenium
(2) Tungsten
(3) Gold
(4) Aluminum
(5) Aluminum oxide
(6) Zirconium dioxide
(7) Boron nitride

All of these materials except gold and aluminum are more refractory than platinum, and it was expected that the gold and aluminum would form high-melting-point intermetallic compounds with the substrate metals.

These materials and the basis for selection of each are more thoroughly discussed in a later section of this report.

III. COATING METAL OXIDATION

A. General Discussion

A review of literature produced at least 13 papers concerned with the mechanism and rates of platinum and rhodium oxidation published since 1957 (Ref. 3-14). While a number of variables affecting the oxidation rates have been identified, the complex problem of separating their effects quantitatively remains.

The work of Alcock and Hooper (Ref. 5) and of Shafer and Tebben (Ref. 7) indicated that the oxidation of platinum and rhodium at high temperatures occurs at a linear rate through the formation of their respective volatile oxides - PtO_2 and RhO_2. The type of reaction taking place is shown below.

$$Pt\ (solid) + O_2\ (gas) = PtO_2\ (gas)$$

Important factors affecting the rate of oxidation and, therefore, their subsequent losses of weight as volatile oxides are:

1. Temperature. Oxidation rate increases with increasing temperature.

2. Oxygen pressure. Oxidation rate increases with increasing oxygen pressure.

3. Flow rate of oxygen over the sample. Oxidation rate increases with increasing flow rate.

4. Degree of saturation of the atmosphere above the sample with the respective volatile oxide. Oxidation rate increases with decreasing saturation of the atmosphere with the respective volatile coating oxides.

It is interesting to note that the fourth factor, the degree of saturation of the atmosphere above the sample with volatile oxide, may lead to variations in oxidation rate with sample placement, size, and shape. It is worth noting that very large differences in oxidation rates have been found in the literature for platinum and rhodium, and it appears virtually certain that this factor is predominantly responsible.

Platinum and rhodium have very similar volume oxidation rates at high temperatures and, therefore, neither constituent is lost preferentially from any of these alloys. Addition of rhodium to

platinum has the added advantage that it raises its melting point, although it decreases its ductility to the point where alloys containing above 40% rhodium are not considered workable (Ref. 15).

B. Coating Metal Oxidation Experiments Conducted in This Program

Because, as indicated above. the effects of the factors controlling platinum and rhodium oxidation rates are not fully understood quantitatively, a series of oxidation experiments were included in this program. The purpose of this work was to provide data from tests which would be performed under conditions that would be duplicated in later tests on composites; i.e., base line data, and to indicate to what extent certain variables - air flow, specimen position, and humidity - might affect the oxidation rate. The tests that were run may be divided into three categories according to the variables investigated:

1. Rate of oxidation as a function of temperature and air flow rate.

2. The effect of specimen position on rate of oxidation.

3. The effect of humidity on rate of oxidation.

C. Tests

The oxidation test setup used in these experiments is shown in Fig. 1. The test furnace is a horizontal tube furnace using a silicon carbide spiral heating element enclosing a 1-1/4 inch ID mullite combustion tube. The furnace temperature was controlled to $\pm 20^{\circ}F$ at $2550^{\circ}F$. The coating test samples had dimensions of approximately 1 inch by 3/4 inch by 0.005 inches. They were admitted to the furnace for testing in alumina combustion boats. Specific details of the respective tests are presented below.

1. Rate of Oxidation Loss as a Function of Flow Rate and Temperature

The initial tests in this study were conducted at $2200^{\circ}F$ and $2550^{\circ}F$ in air flows of 24 and 240 ipm (linear flow rate at room temperature and pressure) for comparison with data obtained by Battelle (Ref. 9) and by General Electric (Ref. 11). Later some of the flow rate data was extended to 480 and 960 ipm, and a single test was made at $2800^{\circ}F$ with an air flow rate of 24 ipm.

In early tests two samples were tested at a time, but when the differences in oxidation rates of the samples indicated that position would have a significant effect, the testing was limited to one sample at a time. The results of the tests on these single samples are given in Table V.

An interesting comparison can be made between the data obtained in the course of this program and the data obtained by Battelle (Ref. 9) and General Electric (Ref. 11), through the use of an Arrhenius plot, as in Fig. 2. The oxidation data obtained in this program compares favorably with that of General Electric at a flow of about 240 ipm. However, data obtained at an air flow of 24 ipm differs significantly from that obtained by Battelle at a similar flow rate. A likely source of this discrepancy is the difference between the surface areas of the samples used here and those used at Battelle. The specimens used in their program were 6 to 9 inches long by 0.7 to 0.4 inches wide by 0.003 inches thick and they were coiled around the post of a quartz suspension basket for testing. They were, therefore, relatively large samples when compared to the 0.500 inch by 0.500 inch by 0.02 inch samples used by General Electric, or to the rectangular 1 inch by 3/4 inch by 0.005 inch samples of this program. The Battelle samples, then, had about 10 times as much surface area as the samples used in this program and 30 times as much as the samples used by General Electric. Increases in surface area, particularly at low flow rates, will cause corresponding increases in the concentration of oxide vapor (increases in the degree of saturation) in the air directly above the sample. This, in turn, will result in oxidation losses which will be lower than those obtained under conditions where the oxide concentration is lower. Differences due to this factor, as previously pointed out, can be quite large (>factor of 2) and both Betteridge and Rhys (Ref. 6) and Hill and Albert (Ref. 12) have emphasized this point.

It is interesting that the slopes of the Arrhenius plots in Fig. 2 are quite similar. This indicates that the activation energies are nearly equivalent, as might be expected. Due to differences or insufficient specification of testing conditions, the oxidation rates obtained by Fryburg and Petrus (Ref. 8), Hill and Albert (Ref. 12), and by Phillips (Ref. 13), are not directly comparable with those presented in Fig. 2. However, in the absence of anything that might catalyze or inhibit the oxidation reaction, the activation energies obtained from their data should essentially match those obtained from the plots of Fig. 2. The activation energies from all these sources are presented in Table VI.

Only one value, that reported by Phillips (Ref. 13), differs greatly from the others. The uniformity and linearity of the oxidation rates found in his published data indicate that his experiments were well controlled and the cause of the variance is not evident.

As shown in Table V, at 2550°F platinum oxidation loss rates were obtained for four different air flow rates. The significance of this data is more clearly seen in the plot of loss rate as a function of air flow rate shown in Fig. 3. The rate of oxidation weight loss is seen to increase with increasing rate of air flow, but at a diminishing rate, so that a virtually constant rate of weight loss is obtained at air flow rates above 960 ipm. This relationship has been established for only one level of temperature, namely 2550°F, but it appears reasonable to assume that it would

hold true for other levels of temperature, although the levelling off would likely occur for some other value of air flow rate. This behavior has been attributed to the belief that weight loss at high air flow rates is controlled by the rate of oxide formation rather than by the availability of oxygen for the reaction, or removal of the oxidation products, as is the case at low air flow rates.

As was noted in the preceding section, position has a readily observable effect on the rate of oxidation. Since it was found convenient to conduct tests on the coating-base metal composites three-at-a-time, an investigation into the positioning effects was undertaken. Figs. 4 and 5 show the variations in rates resulting from some positioning differences with platinum samples at 2550°F in a 240 ipm air flow. For three samples leaning against the sides of the alumina combustion boat, as in Fig. 4, all of the samples have oxidation rates (weight losses) lower than that of singly tested samples. Also, the sample farthest upstream in the air flow has the greatest rate of oxidation, and the one farthest downstream has the lowest - over 50% lower than would be expected for a singly tested sample. This gives some indication of how important a factor the degree of PtO_2 saturation of the atmosphere can be.

Another test, conducted with three samples lying flat across the top of the combustion boat produced some additional interesting data on the effect of position - as shown in Fig. 5. While, as in the previous experiment, the oxidation rates are seen to decrease from upstream to downstream, the rate is much higher with the flat-lying upstream sample which has an oxidation rate actually 35% higher than expected for a singly tested leaning sample and 70% above the leaning upstream sample from the test which included three leaning samples. It is likely that these positioning effects would not lead to as great differences in oxidation rates at higher flow rates; however, this supposition has not been confirmed.

3. The Effect of Humidity on the Rate of Oxidation

Previous studies of the oxidation of platinum metals in flowing air have generally used dry air. No reference was found, however, to indicate whether or not moisture might have any influence on the rate of oxidation of the platinum metals. As the proposed oxidation-resistant platinum coatings would likely be expected to offer protection in air with varying degrees of moisture content, it was decided that the effect of humidity, if any, on the high temperature oxidation of platinum should be determined.

Two tests were conducted, one at 2550°F and the other at 2200°F. For each test, the air used was bubbled through water at room temperature just prior to entry of the test furnace at a flow

rate of 24 ipm. The water picked up in the process (gas and liquid) was found to raise the dew point of the air to about 120°F, whereas the dew point of air used in our previously discussed oxidation experiments has been about -40°F. Dew points were measured after the air passed through the furnace. The results of these tests showed the increase in humidity to produce no corresponding increase in the rate of oxidation. Apparently, the platinum and water vapor do not react under these conditions. The test results are given in Table VII in comparison with results obatined in dried (-40°F dew point) air.

D. Discussion of Results

On the basis of the data obtained in this investigation, platinum or platinum-10% rhodium coatings 2 to 3 mils thick are capable of providing oxidation resistance far in excess of the program objective of 100 hours at temperatures up to 3000°F, providing diffusion-induced degradation problems can be overcome.

While platinum is very expensive and, at present prices ($90 per ounce), with a square foot of platinum coating material 2 mils thick costing about $300, in some cases it could be used very economically. One possible use would be on leading edge material for a re-usable space vehicle, where its low emissivity and its low oxidation rate at low oxygen pressures would be important.

The oxidation resistance of the platinum-10% rhodium alloy did not appear to be significantly greater than that of pure platinum. On the basis of oxidation resistance alone, then, the higher cost of the alloy would not be justified. Other properties, such as improved hot strength, compatibility with the substrate and melting point, may warrant its use in some cases.

IV. COATING-BASE METAL COMPOSITES

A. General Discussion

Platinum and the platinum-rhodium alloys are ruled out as basic materials for refractory structural members because they have a comparatively low strength-to-weight ratio at high temperature and would be too costly in any event. However, in view of their excellent oxidation resistance and ductility, it is somewhat surprising that they have received only a small amount of attention as possible high temperature oxidation-resistant coatings. There are, apparently, two reasons behind this lack of attention: (1) the high cost of the material, and (2) a feeling by many that oxygen would rapidly diffuse through platinum at high temperatures.

As has been pointed out in the preceding section of this report, there is little doubt that platinum and platinum-rhodium oxidation rates are sufficiently low to make their use economically feasible for many applications. In the absence of diffusion-induced coating failure or incompatibility of coating material with substrate, the coating materials should easily meet the ambitious coating requirements of this program.

Rhys (Ref. 16) investigated rather thick platinum coatings (almost 20 mils thick) for high temperature oxidation protection of molybdenum rods and substantiated the existance of a diffusion problem leading to greatly reduced protective lives for platinum coatings on molybdenum. To overcome the diffusion problem he sought diffusion barrier materials for use between the platinum and molybdenum to stop the possible inward diffusion of oxygen and/or outward diffusion of molybdenum. Alumina and gold were used with some degree of success at 2200°F, although his coatings had protective lives far short of what might be expected with the complete absence of diffusion.

The diffusion problem remains, then, a primary impediment to the use of platinum or platinum-rhodium alloy coatings for the high temperature oxidation protection of refractory metals.

Only one other study of platinum or platinum-rhodium alloy coatings for high temperature oxidation protection of refractory metals was found in the literature (Ref. 17), and the electroplated coatings on molybdenum for that investigation were too porous for accurate appraisal of the coating capability.

While the diffusion problem has not been clearly defined, it appears that the idea of oxygen diffusing through a pure platinum coating to oxidize a refractory metal substrate is not correct. Norton (Ref. 18) has shown oxygen diffusion in platinum to be very low at 2600°F. In addition, later work by Betteridge and Rhys (Ref. 6) indicated that diffusion of oxygen through pure platinum would not lead to oxidation of tungsten or molybdenum. However, Betteridge and Rhys did show

that oxygen does diffuse through platinum alloyed with small amounts (about 2%)of either tungsten or molybdenum, and that internal oxidation does occur in these alloys.

Although, on the basis of the work discussed above, it was almost assured that it would be necessary to develop diffusion barriers for use between the platinum coatings and substrate materials, additional work on coating-base metal composites was considered desirable and was undertaken with two objectives in mind:

(1) To determine just how good the respective coating-base metal combinations were - providing "base line data" to be used for comparison with the results of tests on samples containing diffusion barriers.

(2) To obtain a better understanding of the coating failure mechanism and, therefore, perhaps to provide a better insight into what materials and modifications would best improve the respective composites.

B. Preparation and Testing of Samples

No difficulties were encountered in roll bonding the prescribed coatings and substrate metals. However, coating samples without edge protection were found to fail too rapidly in testing to give useful information. Because of this, several techniques of applying edge protection were considered and used to prepare samples. On the basis of the results of tests on these early samples, a technique was devised whereby the base metal was hermetically sealed within the coating. This was done by etching away base metal at the sample edges with an acid solution ($40HF\text{-}30HNO_3\text{-}30H_2SO_4$) and hot press bonding the resultant overhanging coating metal layers together. The first test samples prepared by this method were discs 1-1/4 inch in diameter and 20 mils thick, which had to be bent to allow admittance to the 1-1/4 inch ID tube of the test furnace. Later samples, prepared using the setup shown in Fig. 6, were rectangular in shape, 1 inch long by 3/4 inch wide by 20 mils thick. These samples had about the same surface areas as the coating metal oxidation test samples and were easily admitted to the test furnace.

High temperature structural applications of the refractory metals commonly use sheet in the range of 10 to 60 mils thick. Therefore, the coatings to be used must be kept fairly thin in order to maintain a satisfactory strength-to-weight ratio. For this reason, the coatings prepared for this investigation have been limited to 2 to 4 mils thick. Cost considerations would also dictate that minimum practical thicknesses be employed.

The same oxidation test equipment used for the coating material oxidation tests was used for the study of the composites.

In early tests platinum and platinum-10% rhodium clad FS-85 and TZM test samples were tested singly. Temperature and air flow conditions were similar to those used in the coating metal tests, with most of the tests being conducted at 2550°F in a 24 ipm air flow. 2550°F seemed most appropriate as a test temperature since it is at about this temperature that the oxidation resistance of the silicide and aluminide coatings are seen to become particularly inadequate.

In the course of testing, the samples were cooled to room temperature and examined for weight and surface changes in cycles of one to three hours. The following observations were derived from these initial tests:

(1) Oxidation of FS-85 clad with platinum or platinum-10% rhodium occurs through the penetration of the cladding by oxygen, resulting in the localized formation of oxide beneath the cladding surface. The diffusion of oxygen is believed to occur only after the coating layer has been altered by diffusion. This oxide buildup increases the weight of the sample during testing and produces blisters beneath the cladding which eventually break, exposing the base metal oxide. Until these breaks occur, however, the weight-loss rate is essentially identical to that for the coating material alone.

(2) Oxidation of TZM clad with platinum or platinum-10% rhodium occurs through diffusion of molybdenum to the cladding surface where it is removed as oxide vapor, leaving discontinuous voids beneath the coating. As a result of this permeation of the platinum by the molybdenum, the weight-loss rates for these composites become significantly higher than those obtained for the coating metal alone.

Most of the early tests will be ignored in this discussion, as imperfect edge protection procedures used in the preparation of the test samples often led to erratic gains and losses of weight in the course of testing and resulted in some uncertainty in the identification of coating failure times. Only one of the early tests is felt to have sufficient merit for discussion here, primarily because the sample appeared to be well sealed and it was conducted at 2200°F - a temperature not used in later tests. The weight changes versus time at temperature obtained for that test are presented in Fig. 7. If failure is to be indicated by the first appearance of oxide blisters on that FS-85 base sample, the coating had a protective lifetime of 49 hours.

As the sample preparation technique was perfected and more knowledge was gained as to the mechanism of coating failure, a more sophisticated testing and evaluation procedure was devised. Initial oxidation tests at 2550°F showed diffusion induced coating failure to be so rapid that coating thickness losses were negligible. Therefore, positioning had virtually no effect on the protective lifetimes of coatings on samples tested at the same temperature. Thus it appeared

that several composites might be tested at once under equivalent conditions of time and temperature, thereby speeding up testing. On this basis it was decided that three samples would be tested at a time: (1) a coating/FS-85 sample, (2) a coating/TZM sample, and (3) a platinum sample to serve as a standard for comparison. For these tests, samples were heated in a 240 ipm air flow at 2550°F for one-hour periods until failure occurred. Observations of weight and surface changes were made at room temperature following each hour of exposure.

It was planned that the tests would be made first with platinum coatings and then with platinum-10% rhodium coatings. However, as previously mentioned, a batch of platinum obtained for the preparation of test samples was found to contain about 2.5% palladium as an impurity. In deciding whether or not the palladium contamination present in this material should rule out its use, the properties of palladium were considered closely.

Palladium has been reported to have a weight-loss rate in air approximately equal to that of platinum at 2370°F, but with increasing temperature the rate increases well above that of platinum. Also, its weight losses in air do not indicate its true rate of oxidation which may be obscured because of its -

(1) Volatility. Its weight losses in nitrogen at 2730°F are about five times that for platinum in air at that temperature (Ref. 12).

(2) Permeability to oxygen. It has an oxygen solubility of 0.63% at 2200°F (Ref. 6).

As a further shortcoming, its melting point is only 2830°F.

It was believed, however, that these deficiencies might be of little significance when the palladium was present in as small a quantity as was found here. In view of this, and the delay expected in obtaining pure platinum, it was felt that samples with the impure coatings would be useful in the development and improvement of the testing and evaluation techniques. Platinum of satisfactory purity was subsequently received for the further evaluation of the binary composites.

In early tests, changes in rate of weight loss were considered the best indications of coating failure. However, it was difficult to use this criteria on the platinum-2.5% palladium clad samples, and the tests were conducted to well beyond what was later acknowledged to be the point of coating failure. The difficulty arose from the preferential loss of palladium from the coating, yielding a weight-loss rate initially much higher than for pure platinum, which decreased with time at temperature as palladium was depleted from the alloy by volatilization.

Fig. 8 shows weight loss as a function of time for the pure platinum standard and for the platinum-2.5% palladium clad FS-85 and TZM samples at 2550°F in a 240 ipm air flow. Fig. 9 shows the same relationship for a sample of platinum-2.5% palladium tested singly under similar conditions of temperature and air flow.

In order to help show how oxygen had affected the samples, both externally and internally, the tests described in the paragraph above were re-run in nitrogen, producing some very interesting differences in sample surface condition. The relation of weight change with time obtained in these tests is shown in Figs. 10 and 11. Pictures of the surface condition of the platinum-2.5% palladium clad FS-85 and TZM samples and the platinum-2.5% palladium sample subsequently tested in air are shown in Figs. 12, 13, and 14 at the beginning of testing. The platinum-2.5% palladium clad FS-85 and TZM samples are shown with the platinum-2.5% palladium sample, at their respective failure times in Figs. 15 and 16, and Figs. 17 and 18. Pictures of samples tested similar lengths of time in nitrogen are shown in Figs. 19, 20, 21, 22, 23, 24, and 25. Grain boundaries are readily apparent after testing as a result of thermal etching.

The platinum-2.5% palladium clad FS-85 sample tested in air is seen to have a surface appearance differing little from that of pure platinum or platinum-2.5% palladium, except for water droplet-like spots on the surface of the composite which were found to originate from "rolled in" surface impurities. The sample tested in nitrogen, however, is substantially different, as small crystals are seen to have formed on its surface. In passing, it is worth noting that "rolled in" surface impurities were virtually eliminated after this point as a result of scrupulous care of rolling equipment.

Unlike the FS-85 base sample, the platinum-2.5% palladium/TZM sample tested in air does not have a surface appearance similar to that of pure platinum or platinum-2.5% palladium. Its surface appearance is irregular, almost as though it had been "shot peened." The sample tested in nitrogen, like the FS-85 base sample, is covered by many small crystals.

Observations made on the samples tested in nitrogen showed surface crystal formation to begin after just a few hours of testing - long before the time required to produce coating failure. The uniform distribution of the crystals on both of the coating clad FS-85 and TZM samples tested in nitrogen indicates that intergranular diffusion did not predominate.

The only notable surface changes that have been seen on pure platinum samples in the course of testing were grain boundary shifts.

For the tests on platinum and platinum-10% rhodium clad samples it was considered desirable to discontinue testing as soon after coating failure as possible so that destructive evaluation procedures, such as metallographic examination of sample cross sections, might be used

to identify some of the internal conditions associated with sample failure. The following criteria were used to identify the time of coating failure:

(1) For FS-85 base samples, failure was considered to have occurred when either blisters appeared in the coating or when a weight gain was noted.

(2) For TZM base samples, failure was considered to have occurred when the rate of weight loss was seen to be at least three times that for the coating material alone.

It should be noted that a weight increase equivalent to the sensitivity of the balance used, 0.1 mg, could produce a cube of columbium oxide with sides of about 3 mils. Also, a loss of 0.1 mg from a TZM-base sample would be equivalent to a 2-mil cube of molybdenum. Therefore, significant changes may take place in the course of testing at spots along the coating-substrate interface without any significant difference in rate of weight change, and the time at which oxidation of the base metal begins is difficult to identify with great exactness.

The platinum and platinum-10% rhodium clad samples were tested in the same manner as the platinum-2.5% palladium clad samples except that testing was stopped at their respective coating failure times as determined by the criteria presented above. Time versus weight-loss plots for platinum clad and pure platinum samples, tested together in air and similarly in nitrogen, are given in Figs. 26 and 27. Pictures of the surfaces of samples tested in air for the beginning of testing and at coating failure are presented in Figs. 28, 29, 30, and Figs. 31, 32, 33, and 34, respectively.

Pictures of the samples tested in nitrogen under similar conditions are shown in Figs. 35, 36, 37, 38, 39, 40, and 41.

The time versus weight-loss plots for pure platinum and platinum-10% rhodium clad samples tested in air, and for a pure platinum-10% rhodium sample tested singly under similar air flow and temperature conditions, are given in Figs. 42 and 43. Plots for samples tested in the same manner in a nitrogen atmosphere are given in Figs. 44 and 45. Pictures of the samples tested in air for the beginning of testing and at coating failure are presented in Figs. 46, 47, and 48, and Figs 49, 50, 51, and 52, respectively. Pictures of samples tested in nitrogen under similar conditions are presented in Figs. 53, 54, and 55, and Figs. 56, 57, 58, and 59.

Although only a limited number of tests have been made it appears that no coating-substrate combination tested could be considered significantly superior to the others. Protective coating lives of only 5 to 15 hours were attained at 2550°F - well below the 100 hours at 3000°F goal of this program and about two orders of magnitude below the life that would be expected in the total absence of

diffusion. It is important to note that in spite of the fact that samples were subjected to rather severe thermal cycling in the course of testing, no deterioration or deformation other than noted was observed in any of the composites.

While increases in coating thickness should produce some increase in coating life, it is considered doubtful that economically and structurally usable increases (a few mils or less) would provide the required oxidation resistance at the 2550°F test temperature or above.

C. Evaluation of Binary Composites

Microsections of the twelve binary composites described in the previous section were examined to determine how coating failure occurred. The evaluation included: (1) metallographic examination, (2) electron beam microprobe traverses across the coating-base metal interfaces, and (3) microhardness traverses across the coating-base metal interfaces. The procedures used and results obtained from the examinations are presented below.

1. Metallography

Serious problems were encountered in metallographic work on all twelve samples. These problems were primarily due to the extreme differences in hardness and chemical reactivity encountered among the various coatings and base metals, and their reaction products. Also, it was difficult to keep the edges of the samples from "rounding off" due to spaces left between samples and mounting medium in the mounting process.

The following metallographic preparation technique was found to be the best yet devised for the composites under consideration:

a. A small molybdenum clamp is used to press 5-mil-thick gold foil to each sample face - the soft gold will conform to the edges of the coating material and will withstand any subsequent etching or etch polishing about as well as the coating, therefore providing good protection against rounding off of the edges.

b. The enclosed sample is mounted and ground down with a belt sander until the entire coating-base metal interface is well exposed.

c. The sample is finished through 240, 320, 400, and 600-grit wet papers.

d. The sample is polished first with 6 and then with 1 micron diamond on a napless cloth-covered wheel, using kerosene as a lubricant.

e. Final polishing is done on a napless-cloth-covered wheel with a paste made of .03 micron alumina and 5% chromic acid.

f. Etching is accomplished with hot aqua regia or through the AC electrolytic-cyanide etching technique (5% potassium cyanide solution) usually used on gold.

The samples were examined at magnifications up to 1600X and pictures were taken.

Micrographs of the platinum-2.5% palladium, platinum, and platinum-10% rhodium clad FS-85 samples after testing in air and nitrogen are presented in Figs. 60 and 61, Figs. 62 and 63, and Figs. 64 and 65, respectively. Micrographs of the similarly clad TZM samples after testing are presented in Figs. 66 and 67, Figs. 68 and 69, and Figs 70 and 71. Before considering these micrographs, it should be noted that the polishing and etching techniques are not sufficiently well developed, so that variances between samples with the same substrate metals may in some instances be due to etching differences. The interpretations arrived at in this study are the result of laborious efforts of polishing and etching which are virtually impossible to adequately characterize in photomicrographs. The compound layers at the interfaces of all combinations are easily seen on most of the samples although the TZM samples, except those clad with platinum, are over-etched to such an extent that only one compound layer is seen. The platinum clad TZM samples show three layers. The probable compounds to be found in these samples, based on the major alloying constituent combinations; i.e., platinum-columbium, platinum-tantalum and platinum-molybdenum, are given in Table VIII. The respective phase diagrams are given in Figs. 72, 73, and 74.

Samples tested both in air and in nitrogen appear very similar. The only major differences discernable being the points of coating failure - "blisters" of oxide powder, as shown in Fig. 75 for an FS-85 base sample and "void" areas, as shown in Fig. 76, for a TZM base sample. It is interesting to note that the "void" areas contained small amounts of molybdenum and titanium oxide. Neither the "blisters" in the case of FS-85, nor the "voids" in the case of TZM were found in samples tested in nitrogen for equivalent periods of time.

The etched samples were closely inspected at the coating surface for signs of a build-up of substrate elements such as must have been responsible for the crystals found on the samples tested in nitrogen. A heavily etched surface layer of the type shown in Fig. 77 was found on several of the TZM base samples tested both in air and in nitrogen, but none was found on the FS-85 base sample. It may be that the layer had been lowered to such an extent by etching that it was not observable.

2. Electron Beam Microprobe Analysis

The electron beam microprobe work was performed under subcontract by Advanced Metals Research Corporation. Only the platinum clad samples were examined, as it was felt that the distribution of an additional coating element in the case of platinum-10% rhodium would complicate the analysis without providing additional information of much consequence.

The samples subjected to microprobe analysis were in the "as polished" condition, such that the diffusion layers were not so easily distinguishable as after etching.

Most of the layers found in the course of metallographic examination of etched cross sections were identified in the microprobe work. All of these are compounds which are found among those listed in Table VIII. However, it was difficult to associate some of the layers with specific compositions or compounds because they were very thin. Also, they could not be definitely determined from the literature on which the information in Table VIII was based.

The compositions and compounds identified in the platinum coated samples have been denoted beside the appropriate layers in their micrographs, and where the identity of a compound in a layer was uncertain, a hypothetical compound has been given with a question mark in parentheses (?) beside it.

From the point just beyond the outermost diffusion layer to the sample surfaces only pure platinum was detected. However, a high concentration of titanium was found at the coating surfaces of the TZM base samples which is believed to have been responsible for the crystals which formed on the samples tested in nitrogen. The FS-85 base sample showed no similar buildup of an element at the coating surface, but it was not possible to analyze for zirconium, the element which is considered likely to have been responsible for the crystals formed during testing in nitrogen. On the basis of these findings it is tentatively concluded that the crystals formed were titanium nitrides in the case of the TZM samples, and zirconium nitrides in the case of the FS-85.

It is believed that the major alloying constituents of the base metals were not detected in the outer platinum layer of the coating because of the extremely rapid diffusion rate in that layer as compared to that in the intermediate layers. As minor alloying elements were found at sample surfaces, similar evidence of the outward diffusion of major alloying elements would be expected. Sufficient information has not as yet been obtained to offer an explanation. The microprobe traverse did not cross a grain so that no evidence of compositional differences at the grain boundaries was obtained.

The minor alloying elements, titanium and zirconium (possibly),

are believed to have diffused through the coating by transgranular diffusion in such low concentrations that they were not detectable.

3. Microhardness

Microhardness traverses were made across the interfaces of all twelve test sample combinations in the "as polished" condition. The traverses were made with a Knoop indentor using a 2-gram load.

While the areas of diffusion layers were easily identified, no additional important information was obtained from the microhardness traverses. The data for the platinum and platinum-10% rhodium clad samples is presented in Figs. 78, 79, 80, and 81 and Figs. 82, 83, 84, and 85.

D. Discussion of Results

The metallographic interface examination revealed layers at the area of the coating-base metal in each sample, which had resulted from the diffusion and reactions that took place between the platinum and the substrate metals. All of the layers were well below the coating surface. The defects associated with coating failure were noted in several air tested samples; however, no evidence of peculiar coating features such as porosity, large grain boundaries, or excessive diffusion of base metal into the upper portion of the coating, etc., was noted in these areas.

Microprobe analysis identified most of the compounds in the diffusion layers. None of the substrate metals was detected in the platinum between the compound layers and the surfaces of the samples. However, titanium was detected at the surface of the TZM base samples and it was believed that zirconium was present at the surface of the FS-85 base samples.

Microhardness traverses provided no additional useful information.

On the basis of these examinations it is believed that coating failure occurs after a relatively low percentage of substrate alloy reaches the surface of the coating, forming a path through which (1) oxygen may rapidly penetrate the coating in the case of the FS-85 base composites, and (2) molybdenum may rapidly proceed to the surface and be removed as a volatile oxide from the TZM base composites.

Before this hypothesis can be accepted a great deal of confirmatory evidence will be necessary. Much of the required evidence can probably be obtained by the use of more refined metallographic and microprobe work.

V. DIFFUSION BARRIER STUDIES

A. General Discussion

The diffusion barrier may be thought of as a special layer to be interposed between the coating and the substrate to produce a new "composite coating system" which is more likely to be capable of meeting the prescribed coating objective.

A number of materials were selected for consideration as potential diffusion barriers, primarily on the basis of the following:

(1) Past studies indicating their effectiveness in retarding diffusion.

(2) Chemical inertness.

(3) Melting point.

It was expected that several likely trouble areas, notably expansion mismatch and brittleness, might be reduced in importance through the development of techniques for depositing the barriers as thin flexible films.

The materials which were evaluated may be grouped into three classes, as given below:

1. Metallic Elements and Alloys. Important attributes include ductility and bondability. The work of ManLabs (Ref. 17) indicated only little likelihood that any metal might serve as an effective diffusion barrier.

   a. Rhenium. The best of the metals examined in diffusion barrier studies conducted by ManLabs (Ref 19). This material has been used as a diffusion barrier between molybdenum and platinum in electron tube grids which operate at temperatures as high as 2200°F (Ref. 20). Its melting point is second only to tungsten among the metals.

   b. Tungsten. Although Betteridge and Rhys (Ref. 6) found internal oxidation in platinum alloys containing as little as 2% tungsten, the work at ManLabs (Ref. 17) as well as its high melting point favored its examination. It was, however, finally not included in the present scope of work, because of difficulties in specimen preparation.

2. Intermetallic Compounds. They can be expected to have ductilities and bondabilities intermediate to the other two classes of barriers.

a. Gold (expected to form intermetallics with the coating and/or base metal). An indication that gold might be useful as a barrier came from the work of Rhys (Ref. 16), in which gold interposed between molybdenum and a platinum coating increased the coating's protective life at 2200°F.

b. Aluminum (to form aluminides with the substrate alloys). These are among the more refractory and chemically inert intermetallics.

3. Non-Metallic Refractory Compounds. These compounds in general have great chemical stability and are potentially the best barriers to diffusion; however, they suffer extreme brittleness except as very thin films and are difficult to bond to metals.

a. Boron Nitride. The choice of this material was based on demonstrated chemical inertness (Ref. 21) and the fact that an in-house technique was readily available for its deposition as a thin flexible adherent film on refractory metals (Ref. 22).

b. Aluminum Oxide. This material was selected on the basis of its effectiveness in preventing platinum-molybdenum interdiffusion, as indicated by the studies of Rhys (Ref. 16) at 2200°F.

c. Zirconium Oxide. The chemical inertness of this material when in contact with platinum is unquestionable as it is considered to be an excellent crucible material for platinum melting; however, it is rated as only fair for columbium melting crucibles (Ref. 23).

B. Testing and Evaluation

Initially techniques were sought which could be used in the preparation of hermetic coating-barrier-base metal test samples. It was expected that these samples would be subjected to the same oxidation tests used for the coating/base metal composites, such that direct comparisons could be made to provide an indication of the effectiveness of these barrier materials. The deposition techniques explored included:

(1) Roll bonding.
(2) Hot press bonding.
(3) Vapor deposition.
(4) Electrolytic deposition.
(5) Thermite reaction.

In early studies it became evident that a considerable amount of time would be required for development and testing of acceptable hermetic barrier containing composites. Because of this, it was felt that a screening test was needed which could give some indication of the merit of a barrier without necessitating preparation and testing of hermetic fully-bonded composites. In the test devised for this purpose, a sample of the type shown in Fig. 86 was used. In the preparation of this sample the barrier layer was applied to one face of each piece of substrate metal by one of the deposition techniques given above, and the other face was kept clean. A 2-mil thickness of platinum foil (coating) was then placed on each face of the sample and the assembly was secured in a graphite clamp, which is shown in Fig. 87. A zirconia wash was used to prevent any interaction between the platinum and the graphite. The clamped assembly was then heated in vacuum for 16 hours at 2500°F.

From previous coating-base metal composite tests, diffusion was known to have produced easily discernable compound layers at the coating-substrate interface at 2550°F. It appeared, then, that 2550°F would be an adequate test temperature. However, as the only vacuum furnace available for this testing had a maximum use temperature of 2500°F, the tests were conducted at that temperature.

After testing, the samples were examined metallographically to determine the extent of diffusion on both sides of the sample. With the diffusion barrier applied to only one side of the sample its effectiveness could immediately be determined by comparison with the other face of the sample which contained no barrier layer. The results of these screening tests are given in Table IX.

The techniques used in barrier deposition and the testing of the barriers is discussed further in the following paragraphs.

1. Rhenium

At first, it was thought that rhenium might most easily be introduced as a layer between coating and base metal through a roll bonding technique. However, certain unusual properties of this metal led to difficulties.

Although rhenium is more ductile than the molybdenum alloy which has been easily roll bonded to platinum in the course of this program, it is very difficult to fabricate. The difficulty arises from the high rate at which it work hardens (faster than any other metal); and the fact that it suffers hot shortness, so that hot rolling has not been successfully used to overcome the problem of work hardening (Ref. 24). Reduction is accomplished through cold rolling; light reductions are initially applied, gradually increasing to 40% between anneals at 2900°F in vacuum, hydrogen, or cracked ammonia.

As it was believed that the hot shortness in rhenium resulted from oxide in the grain boundaries, it was thought that the problem might be overcome by doing the hot rolling in an evacuated package.

An attempt to prepare Pt-10Rh/Re/FS-85 composite material for test samples by hot rolling at 1800°F in an evacuated package was unsuccessful. The composite obtained had a dark wavy surface, and metallographic examination showed the rhenium layer to have broken up during rolling, as seen in Fig. 88. It is believed that during rolling the FS-85 and platinum-10% rhodium tended to "flow," while rhenium with its high yield strength could not, and thus broke up.

Two other methods were considered for preparation of samples with rhenium diffusion barriers: (1) electrolytic deposition, and (2) chemical vapor deposition. The former technique was selected as it appeared to have reached a much higher stage of development than the latter.

Summit Finishing Company,which has had previous experience in rhenium electroplating, was contacted and subsequently prepared several samples of rhenium coated FS-85 and TZM for this work. Coating thickness was approximately 0.1 mils in all cases. The samples obtained were used in the screening test described previously and, as indicated in Table IX, metallographic examination showed the rhenium coating to have been ineffective as a diffusion barrier. There are two possible conclusions that may be drawn: (1) either rhenium is not inherently an effective diffusion barrier in the test environment described, or (2) the rhenium electroplate was porous. As no indication of the rhenium phase was apparent in metallographic examination, it is assumed that the former conclusion is correct.

2. Gold

A number of Pt/Au/FS-85 samples were prepared by essentially the same technique developed for making the coating-base metal samples. That is, platinum and gold layers were bonded to either side of a piece of FS-85, from which samples were cut out, undercut with acid, and sealed by hot press bonding of their edges. After a few minutes of heating in flowing air at 2550°F the gold (about 0.9 mils thick) was seen to have formed an alloy with the platinum layer (about 3 mils thick) which had a liquid phase below 2550°F and flowed off portions of the samples, subjecting them to high temperature oxidation. In view of this platinum-gold alloy problem, it was decided that a change in preparation technique would be necessary.

The development of the "screening test" appeared to provide a method which could be used to obtain important information concerning the preparation and effectiveness of gold diffusion barriers at a minimum expense of time and effort. For this test, samples of roll bonded gold on refractory metal were sintered at 1400°F in vacuum in order to form a gold-refractory metal alloy, or compound, which might withstand the 2500°F test temperature without melting. The pre-heat treatment was apparently effective, as the tested samples showed no signs of melting. As indicated in Table IX, however, the gold apparently had little or no effect on the rate of diffusion - evidenced by the presence of the usual diffusion layers. One unusual thing was noted with the FS-85 substrate - a phase layer not previously observed, was found on the substrate side of the other compound layers. Gold, then, is ineffective as a diffusion barrier under the given test conditions.

3. Aluminum

Aluminides, formed from the reaction of aluminum with the coating or base metal, were examined as possible diffusion barriers by means of the screening test.

In order to avoid the possible formation of a platinum-aluminum alloy with a melting point below the test temperature, roll bonded aluminum clad refractory metal samples were diffusion annealed 4 hours at 1200°F in helium prior to testing in order to form the respective refractory intermetallic compounds.

As stated in Table IX, metallographic examination of tested samples revealed diffusion layers, although somewhat different from those usually found, indicating that the aluminide formed was ineffective as a diffusion barrier. It was interesting to note that aluminum deeply penetrated the platinum in the FS-85 base sample, forming a 2-phase region over a mil in thickness beyond the diffusion layer compounds.

4. Boron Nitride

Boron nitride appeared particularly attractive as a potential diffusion barrier material since an apparently excellent method had already been developed for its deposition as a thin flexible film on refractory metal (Ref. 22).

Boron nitride coatings were applied to material for test samples through the decomposition of trichloroborazole on the surface of heated TZM and FS-85 alloy strip. The thickness of the boron nitride layer was estimated to be 0.06 mils.

Sputtering seemed to be the most convenient method for application of the platinum coating layer to form test samples. Through

sputtering the platinum could be deposited on freshly laid down boron nitride with a minimum exposure to atmospheric contaminants and handling that might produce surface damage or inhibit bonding between the coating and diffusion barrier materials.

Two problems were encountered with the sputtering process:

(1) It was difficult to obtain a good platinum-boron nitride bond. This was finally accomplished by post-heating the samples to the melting point of platinum (3223°F) following the sputtering operation.

(2) Only a low deposition rate was attainable through sputtering, necessitating the deposition of additional platinum through some other means.

Pt/BN/FS-85 test samples were prepared by hot press bonding 2-mil-thick coatings of platinum to the thin sputtered coatings (about 0.04 mils thick). The edges of several of these samples were sealed by the usual hot press bonding technique.

It was found that only a few hours of heating in air would cause failure (oxide blisters breaking through the coating) in these samples. However, as failure occurred at the edges of the samples where little or no boron nitride had been deposited, it was thought that this type of sample would not provide a true test of boron nitride as a diffusion barrier.

Metallographic examination of a sample tested in the manner described above revealed diffusion layers not only at the edges where coating failure occurred but across the entire coating-base metal interface. No sign of the boron nitride layer was observable. The failure appeared to be attributable to one of two possible causes:

(1) Degradation of the boron nitride layer due to incompatibility with the platinum and/or FS-85.

(2) Loss of the layer through some process associated with the deposition of the sputtered platinum coating.

In light of the results obtained with the samples described above a different type of test sample was devised. A clearly visible boron nitride coating was deposited on several pieces of the refractory metal alloys for use in these new samples. For these samples the pieces of boron nitride coated refractory metal were vacuum hot press bonded into packages of the type shown in Fig. 89. This sample configuration provided an extra thickness of platinum at the edges of the boron nitride coated refractory metal, thus avoiding the possibility of any rapid sample failure due to diffusion from unprotected edges. A test sample of this type containing BN coated TZM was heated

in flowing air at 2550°F and, as with the previous samples, failed very rapidly with metallographic examination revealing the presence of diffusion layers and absence of any boron nitride.

Although the test results presented above indicated little likelihood of success with boron nitride barriers, test samples of BN coated FS-85 and TZM were subjected to the "screening test" previously described. Metallographic examination of the tested samples revealed only the usual coating-base metal diffusion layers.

5. Aluminum Oxide

Aluminum oxide has long been used as a refractory where contact with hot or even molten metals is required and therefore would be a likely candidate for preventing interdiffusion between the respective coating and substrate metals included in this investigation. In support of this supposition is the work of Rhys (Ref. 16), who showed an alumina layer between a platinum coating and molybdenum substrate to substantially increase the protective life of the coating.

In order to use alumina to help meet the coating requirements of this program, two problems must be overcome:

(1) It must be bonded to both the coating and substrate metals - a difficult ceramic-to-metal joining problem.

(2) It must be deposited as a very thin flexible film in order to overcome its brittleness.

In the course of the program three techniques of aluminum oxide deposition were tried:

(1) Thermite-type reaction - aluminum foil was pressed against the pre-oxidized surface of a piece of refractory metal foil and heated to a temperature sufficient to activate the reaction forming alumina.

(2) High temperature air oxidation of roll bonded aluminum cladding on pieces of refractory metal foil.

(3) Roll bonding alumina powder onto refractory metal sheet.

Neither of the first two techniques produced acceptable coatings - coverage was nonuniform in both cases. The third technique gave coatings of approximately 0.2 mils thickness that appeared to be quite acceptable and the samples produced were subjected to the screening test for diffusion.

Metallographic examination of the samples tested evidenced only the usual diffusion layers - no alumina was discernable at or near

the coating-base metal interface in either the FS-85 or TZM base composites. No explanation can be offered for the disappearance of the alumina layer.

6. Zirconium Oxide

Zirconium oxide, like alumina, is often used in crucibles for melting metals. It is, in fact, considered better than alumina for platinum-melting crucibles and on that basis was selected for evaluation.

Samples of zirconia coated refractory metal were prepared, using the roll bonding technique developed for alumina coatings and these samples were subjected to the "screening test." The zirconia coatings were substantially thicker than the alumina coatings. Actual coating thicknesses were 1.0 mils on the FS-85 samples and 0.7 mils for the TZM.

Metallographic examination of the FS-85 base sample showed that the zirconia layer was ineffective as a barrier to diffusion and that the bulk of the layer was "consumed" during the diffusion test. However, the zirconia layer on the TZM base sample was completely effective in preventing diffusion and it was clearly visible in its "original" condition. The "consumption" of the zirconia layer on the FS-85 sample cannot be explained.

C. Discussion of Results

Screening tests for diffusion at 2500°F for 16 hours showed that, of the 12 combinations obtained from the 6 barrier materials and 2 base metals, only one effective diffusion barrier-base metal combination was found - the $Pt/ZrO_2/TZM$ combination.

The disappearance of the alumina barriers on FS-85 and TZM substrates and of the zirconia on an FS-85 base sample in the course of testing is difficult to explain since no reactions would be expected. These tests should be repeated, preferably with thick barrier layers, before these combinations are acknowledged to be unacceptable. Also, the behavior of aluminum diffusion barriers should be evaluated in air before the abandonment of aluminide barriers, as internal oxidation of the aluminum in the coating or at the coating-base metal interface may occur, forming an aluminum oxide barrier to diffusion.

The three remaining barrier materials - (1) BN, (2) rhenium, and (3) gold - for reasons of incompatibility appear to be of no value in retarding coating-base metal interdiffusion at the 2500°F test temperature.

VI. CONCLUSIONS AND HYPOTHESES

A. Coating Materials Oxidation

1. In the absence of diffusion induced degradation, platinum and platinum-10% rhodium alloy coatings 2 mils in thickness should easily provide over 100 hours of oxidation protection at temperatures up to 3000°F. (A conclusion.)

2. Platinum metal oxidation rates increase with air flow, but at a diminishing rate. Data at 2550°F show that the loss rate has essentially leveled off for flow rates above 960 ipm. (A conclusion.)

3. Water vapor has little or no effect on the rate of oxidation of platinum or platinum-10% rhodium alloy. (A conclusion.)

B. The Mechanism of Coating Failure

1. Diffusion barriers will be required if platinum or platinum-10% rhodium coatings are to meet the objectives of this program - 100 hours of oxidation protection on columbium and molybdenum alloys at temperatures up to 3000°F. (A conclusion.)

2. Failure of platinum and platinum-10% rhodium coatings on TZM in the course of high temperature oxidation occurs by diffusion of the molybdenum to the surface of the coating where it combines with oxygen and is removed as a volatile species. This is, of course, preceded by the formation of the several intermetallic phases. Diffusion proceeds at very rapid rates, such that at 2550°F voids form at the coating-substrate interface in several hours, and grow rapidly with time. Rapid depletion of the molybdenum then takes place with no significant alteration of the external appearance of the sample (assuming it is hermetically enclosed by the coating). Titanium and zirconium also diffuse to the surface where they react to form oxides. That some oxygen diffuses through the coating in the opposite direction is evident from the surface appearance of the voids as well as from the microprobe data. Absence of any "blow-up" failure of these voids would suggest that the rate of oxygen back diffusion is very small and that the bulk of the molybdenum is oxidized at the surface of the coating. It is believed further that, what little oxygen does diffuse, does so only after the coating metal composition has been altered by diffusion, although evidence of this is lacking. (A hypothesis.)

3. Failure of the same coatings on FS-85 under similar conditions occurs in an entirely different way than on TZM. As diffusion of columbium (plus tantalum and tungsten) occurs, a number of intermetallic phases form and grow. As diffusion proceeds, one or more of these elements diffuses to the surface of the coating, where it alters the composition of the coating and allows oxygen to back diffuse toward the coating-substrate interface. Once this path of back-diffusion is established, it proceeds very rapidly in building up a localized area of substrate metal oxide, which equally rapidly results in a blister-like eruption and failure of the coating. Thus it is seen that, unlike the TZM composites which oxidize essentially at the surface of the coating, the FS-85 composites oxidize near the coating-substrate interface. (A hypothesis.)

4. No binary composite of platinum or platinum-10% rhodium alloy coatings with FS-85 or TZM substrates can be considered significantly superior to the others. Protective coating lives of only 5 to 15 hours may be obtained with the combinations for coating thicknesses in the range of 2.5 to 3.1 mils. (A conclusion.)

5. None of the binary composites showed any tendency of accelerated oxidation failure as a result of thermal fatigue. Samples tested cyclically performed essentially the same as those tested statically, demonstrating the value of ductility in protective coatings.

C. Diffusion Barriers

1. One-mil thick zirconium dioxide will stop platinum-TZM interdiffusion at 2500°F for a minimum of 16 hours. (A conclusion.)

2. Failure of alumina diffusion barriers (and their disappearance) cannot be explained, although their structural integrity and small thickness (0.2 mils) are probably responsible.

3. Gold, rhenium, aluminum, and boron nitride are not effective barriers to platinum-TZM or platinum-FS-85 interdiffusion at 2500°F. (A conclusion.)

VII. RECOMMENDATIONS FOR FUTURE WORK

A. Further examination of the coating failure mechanism in binary composites.

B. Development of a technique for deposition of a thin flexible, well-bonded zirconium oxide layer between platinum coating and TZM base metal.

C. Conduct oxidation tests on $Pt/ZrO_2/TZM$ composites.

D. Conduct further studies on other potential diffusion barrier materials.

E. Evaluate composites with the promising diffusion barriers for mechanical property requirements.

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TABLE I

ANALYSES OF THE SUBSTRATE ALLOYS

Composition of FS-85 Alloy

Element	Composition Specification in Weight % (Ref. 25)	Certified Chemical Analysis in Weight %*
Iron	0.01 Max	-
Silicon	0.01 "	-
Oxygen	0.03 "	0.005
Nitrogen	0.015 "	0.0042
Hydrogen	0.001 "	-
Carbon	0.01 "	0.001
Zirconium	0.6-1.1	0.95
Tungsten	10-12	9.8
Tantalum	26-29	27.4
Columbium	Balance	Balance

Composition of TZM Alloy

Element	Composition Specification in Weight % (Ref. 26)	Certified Chemical Analysis in Weight %*
Iron	0.010 Max	0.001
Silicon	0.008 "	0.005
Nickel	0.002 "	0.001
Oxygen	0.0025 "	0.003
Nitrogen	0.002 "	0.001
Hydrogen	0.0005 "	0.0001
Carbon	0.01-0.04	0.02
Zirconium	0.06-0.12	0.10
Titanium	0.40-0.55	0.55
Molybdenum	Balance	Balance

* Certified chemical analyses for the alloys were obtained from the supplier, Fansteel Metallurgical Corporation.

TABLE II

ANALYSES OF PLATINUM AND PLATINUM-10% RHODIUM ALLOY USED IN COATING METAL OXIDATION STUDIES AND IN EARLY TESTS ON COATING-BASE METAL COMPOSITES

Element	Platinum Composition in Weight %	Platinum-10% Rhodium Alloy Composition in Weight %
Si	< 0.001	0.001
Fe	< 0.0005	0.005
Cu	< 0.0005	0.001
Ni	< 0.0005	0.001
Ag	< 0.001	< 0.001
Au	< 0.001	< 0.001
Pd	< 0.0005	0.10
Ir	< 0.001	0.05
Rh	0.47	10.15
Pt	99.53	89.74

TABLE III

ANALYSIS OF PLATINUM OBTAINED FOR COATING-BASE METAL COMPOSITE STUDIES AND FOUND TO CONTAIN PALLADIUM AS AN IMPURITY

Element	Composition in Weight %
Fe	0.02
Cu	0.01
Ni	0.04
Ag	0.36
Au	0.01
Pd	2.41
Ir	0.10
Rh	0.20
Pt	Balance

TABLE IV

ANALYSES OF PLATINUM AND PLATINUM-10% RHODIUM ALLOY USED IN LATER COATING-BASE METAL COMPOSITE STUDIES AND IN DIFFUSION BARRIER STUDIES

Element	Platinum Composition in Weight %	Platinum-10% Rhodium Alloy Composition in Weight %
Fe	-	0.03
Cu	-	0.01
Ni	-	0.03
Ag	0.005	0.01
Au	< 0.01	0.01
Pd	< 0.01	0.10
Ir	0.02	0.02
Rh	< 0.01	9.38
Pt	99.97	90.74

TABLE V

SUMMARY OF EXPERIMENTAL RESULTS FOR THE OXIDATION OF PLATINUM AND PLATINUM-10% RHODIUM ALLOY

Metal	Temperature (^{o}F)	Air Flow (ipm)**	Test Duration (hr)	Linear Rate of Weight Loss (mg/cm^2/hr)	Thickness Loss Per Side (mils/1000 hours)
Pt	2200	24	16	0.014	0.26
Pt-10Rh	2200	24	65	0.010	0.20
Pt	2200	240	17	0.018	0.33
Pt-10Rh	2200	240	17	0.015	0.30
Pt	2200	480	17	0.028	0.51
Pt-10Rh	2200	480	17	0.025	0.49
Pt	2550	24	68	0.045	0.82
Pt-10Rh	2550	24	114	0.040	0.79
Pt	2550	240	17	0.089	1.63
Pt-10Rh	2550	240	17	0.081	1.60
Pt	2550	480	21	0.108	1.98
Pt-10Rh	2550	480	85	0.100	1.97
Pt	2550	960	29	0.121	2.22
Pt	2800	24	17	0.122	2.23
*Pt	3000	960	-	0.71	13.0

* Extrapolated on the basis of the other values, assuming a similar activation energy.

** 1 ipm = 1.06 CFH for the test setup used in this program. Air flow measured at room temperature and pressure.

TABLE VI

ACTIVATION ENERGY FOR THE OXIDATION OF PLATINUM

Temperature Range: 2200-2910°F
Reaction: Pt (solid) + O_2 (gas) PtO_2 (gas)

Reference	Activation Energy (Kcal/Mole)	Air Flow Rate
This Program	38.6	240
This Program	38.0	24
Fryburg and Petrus (Ref. 8)	42.5	Not Given
Battelle (Ref. 9)	42.4	24
General Electric (Ref. 11)	45.7	231
Hill and Albert (Ref. 12)	43.9	0.2 cu ft/tor
Phillips (Ref. 13)	25.4	Not Given

TABLE VII

OXIDATION RATE FOR PLATINUM IN DRY AND WET AIR FLOWING AT A RATE OF 24 IPM

Temperature °F	Dew Point °F	Test Duration	Rate of Weight Loss $mg/cm^2/hr$
2200	-40	16 hr	0.014
2550	-50	68 "	0.045
2200	+120	64 "	0.009
2550	+120	65 "	0.044

TABLE VIII

COMPOUNDS EXPECTED FROM THE INTERACTION OF PLATINUM WITH FS-85 AND TZM ALLOYS AT 2550°F

FS-85

Compounds	
Nb-Pt (Ref. 27)	Ta-Pt (Ref. 28)
Nb_3Pt	-
NbPt	Ta_2Pt*
$NbPt_2$	$TaPt_2$
$NbPt_3$	$TaPt_3$

* Perhaps a mixture of Ta_3Pt and TaPt

TZM

Compounds
Mo-Pt (Ref. 29)
Mo_3Pt
Mo_2Pt_3
$MoPt_2$
$MoPt_3$

TABLE IX

TESTING DIFFUSION BARRIER MATERIALS AT 2500°F FOR 16 HOURS IN VACUUM

Base Metal	Barrier Material	Application Technique	Thickness (Mils)	Test Results
FS-85	Rhenium	Electrolytic Deposition	0.1	Ineffective as a barrier. No new phase layer was apparent.
TZM	Rhenium	Electrolytic Deposition	0.1	Ineffective as a barrier. No new phase layer was apparent.
FS-85	Gold	Roll Bonding - sintered 4 hours in vacuum at 1400°F to develop intermetallic.	0.9	Ineffective as a barrier. A new phase over 1 mil thick appeared on the substrate side of the usual substrate compound interface.
TZM	Gold	Roll Bonding - sintered 4 hours in vacuum at 1400°F to develop intermetallic.	1.0	Ineffective as a barrier. No new phase layer was apparent.
FS-85	Aluminum	Roll Bonding - sintered 4 hours in helium at 1200°F to develop intermetallic.	0.7	Ineffective as a barrier. Layers were present, as usual, at the Pt-base metal interface, but were different in size and appearance from those at the interface where aluminum was absent; also, a 2-phase region was seen where only platinum was normally observed.
TZM	Aluminum	Roll Bonding - sintered 4 hours in helium at 1200°F to develop intermetallic.	0.9	Ineffective as a barrier. Layers were present, as usual, at the Pt-base metal interface, but were different in size and appearance from those at the interface where aluminum was absent - this did not have the same appearance produced with the Pt/Al/FS-85 combination and no 2-phase region was evident.

(more)

TABLE IX
(Contd)

TESTING DIFFUSION BARRIER MATERIALS AT 2500°F FOR 16 HOURS IN VACUUM

Base Metal	Barrier Material	Application Technique	Thickness (Mils)	Test Results
FS-85	Boron Nitride	Chemical Vapor Deposition	0.1	Ineffective as a barrier. No new phase layer was apparent.
TZM	Boron Nitride	Chemical Vapor Deposition	0.1	Ineffective as a barrier. No new phase layer was apparent.
FS-85	Aluminum Oxide	Roll Bonding*	0.2	Ineffective as a barrier. No new phase layer was apparent.
TZM	Aluminum Oxide	Roll Bonding*	0.2	Ineffective as a barrier. No new phase layer was apparent.
FS-85	Zirconium Oxide	Roll Bonding*- sintered 1 hour at 2500°F in helium - to test coating adherence.	1.0	Ineffective as a barrier. Only a little of the original zirconia barrier layer was apparent.
TZM	Zirconium Oxide	Roll Bonding*- sintered 1 hour at 2500°F in helium to test coating adherence.	0.7	An effective barrier. No diffusion appeared to penetrate the ZrO_2 layer.

* A proprietary technique involving the roll bonding of slurry applied coatings.

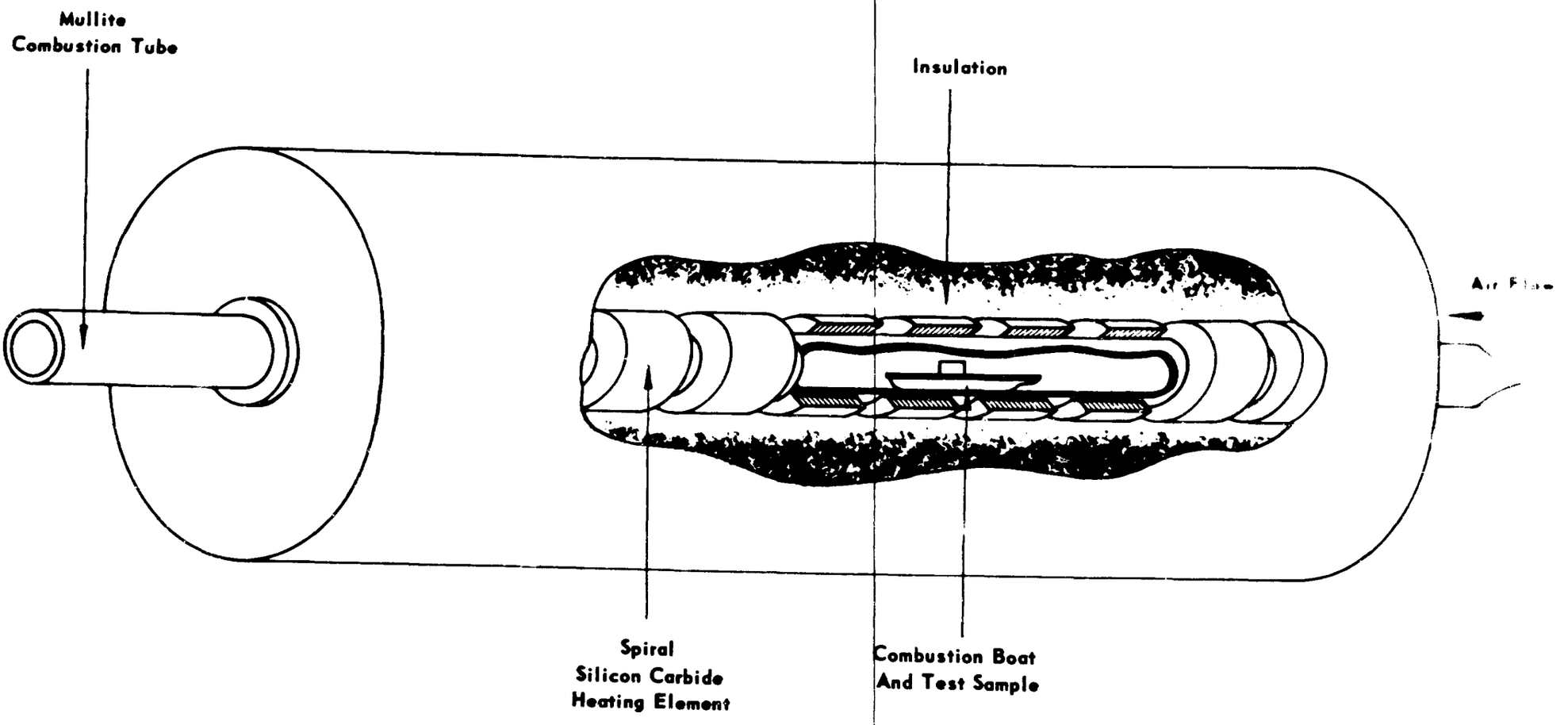


Figure 1 Oxidation Test Furnace

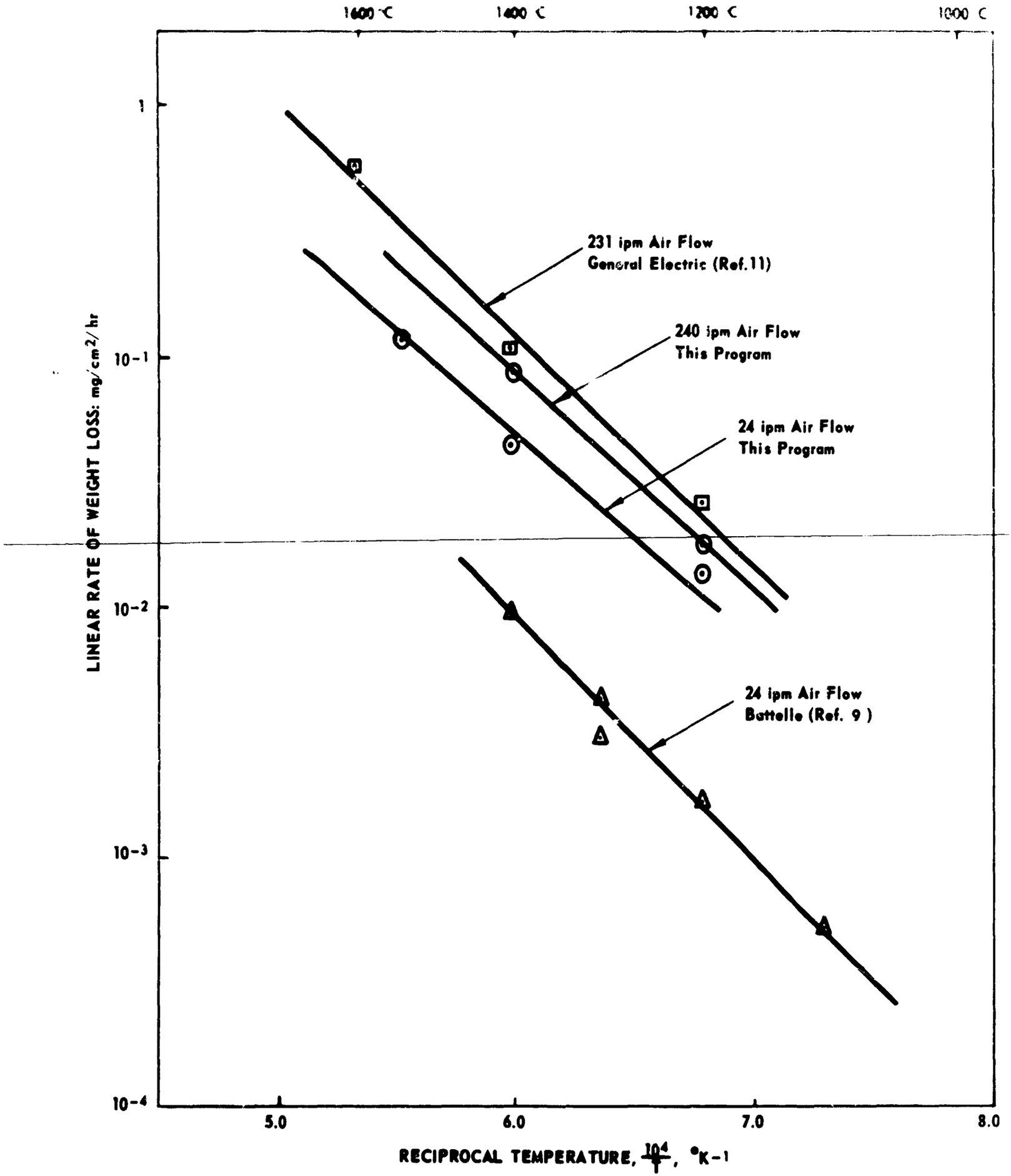


FIGURE 2 Arrhenius Plot of Platinum Oxidation Data.

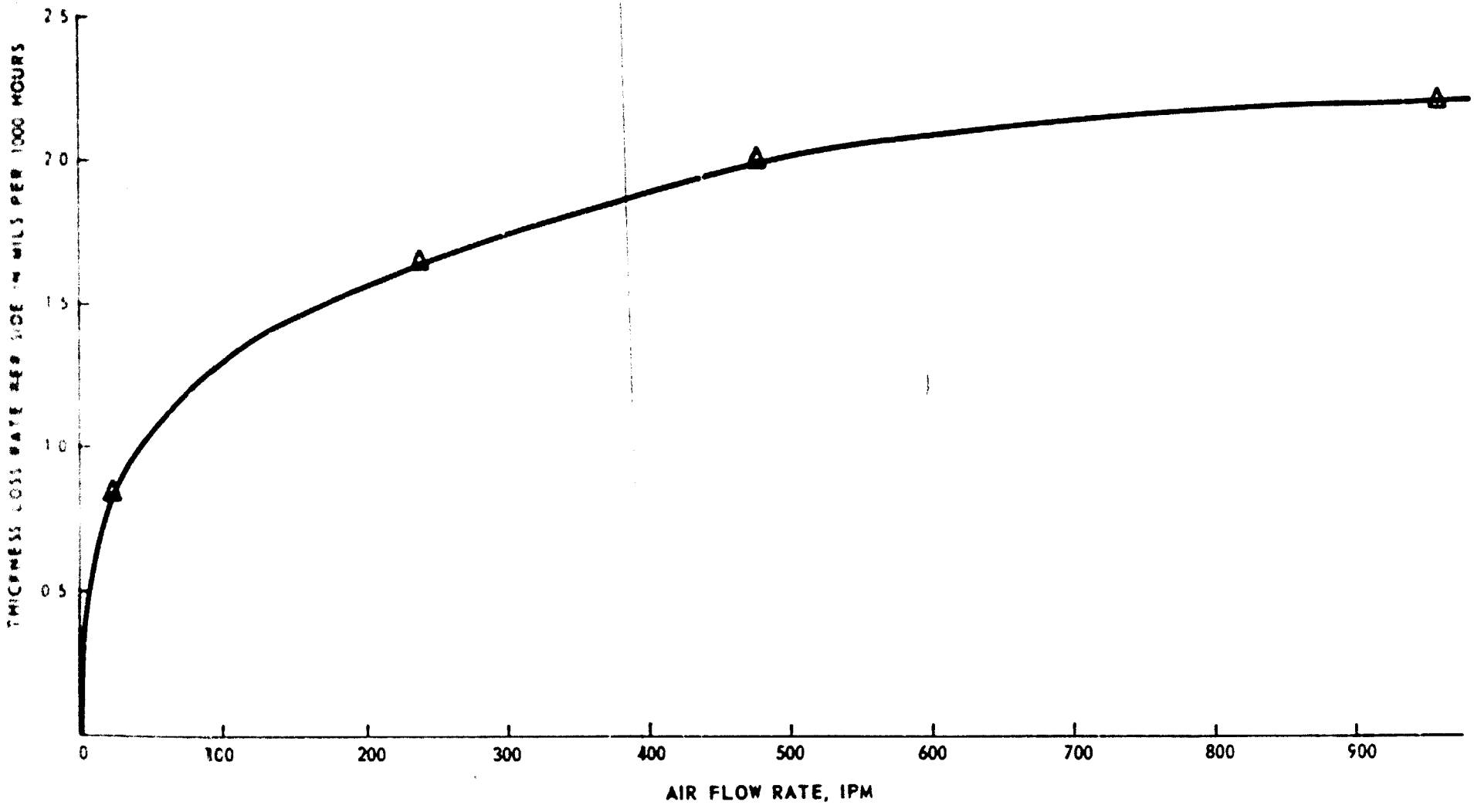


FIGURE 3 Thickness Loss Rate versus Air Flow Rate for Platinum at 2550°F.

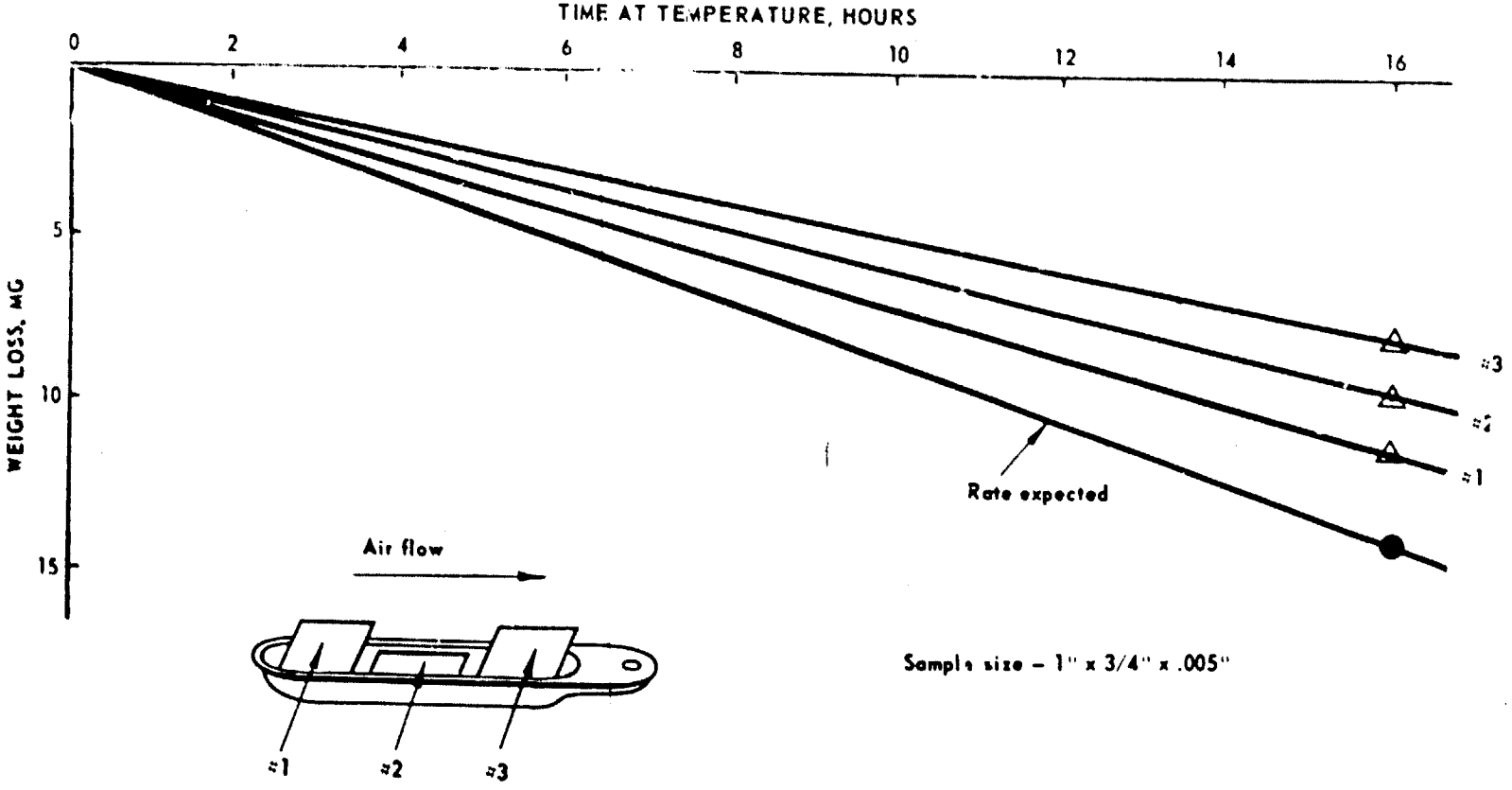


FIGURE 4 Weight Losses for Three Platinum Samples Tested Leaning Against the Sides of a Combustion Boat to Indicate the Effects of Position on Oxidation Rate in a 240 ipm Air Flow at 2550°F

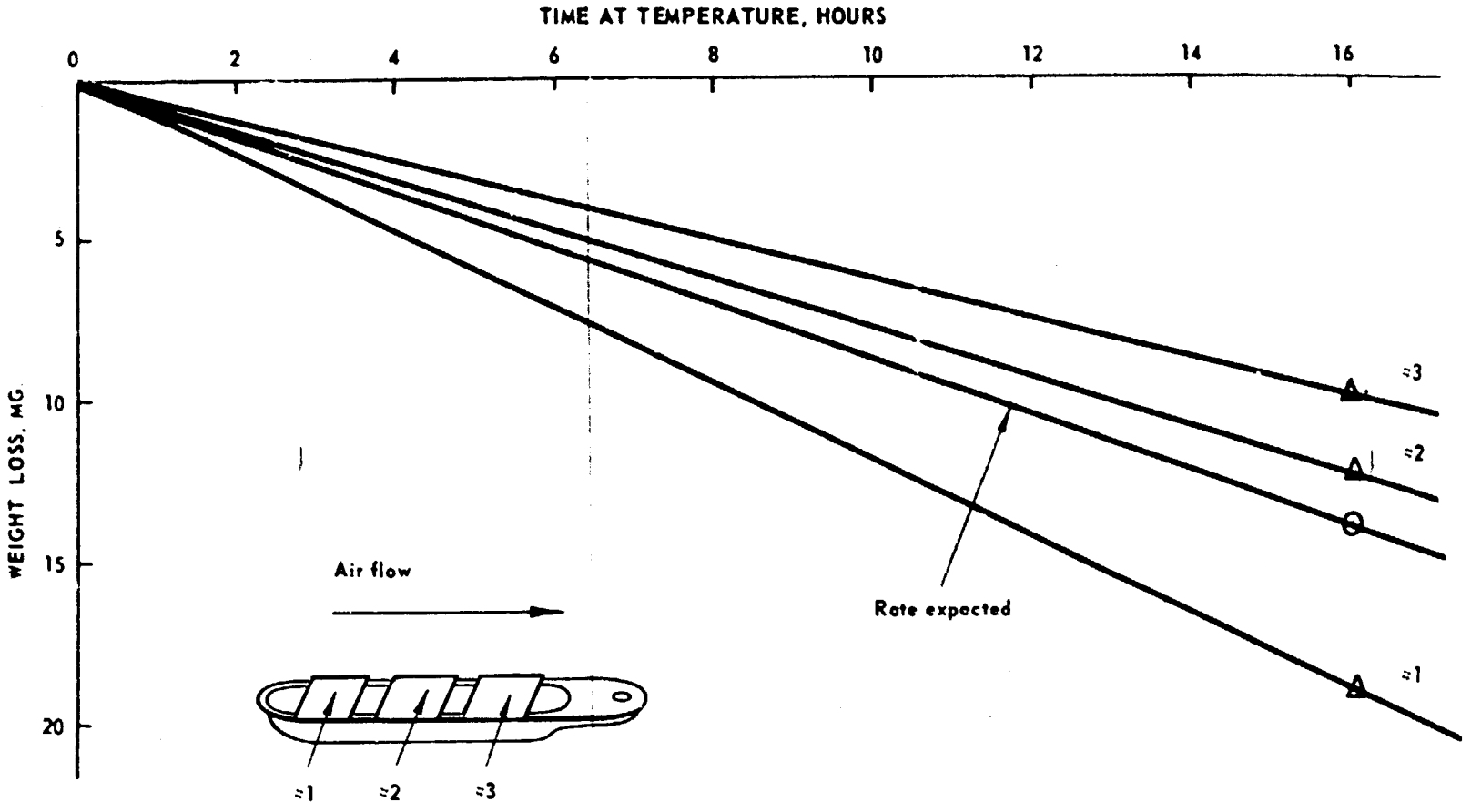


FIGURE 5 Weight Losses for Three Platinum Samples Tested Lying Flat Across a Combustion Boat to Indicate the Effects of Postion on Oxidation Rate in a 240 ipm Air Flow at 2550°F.

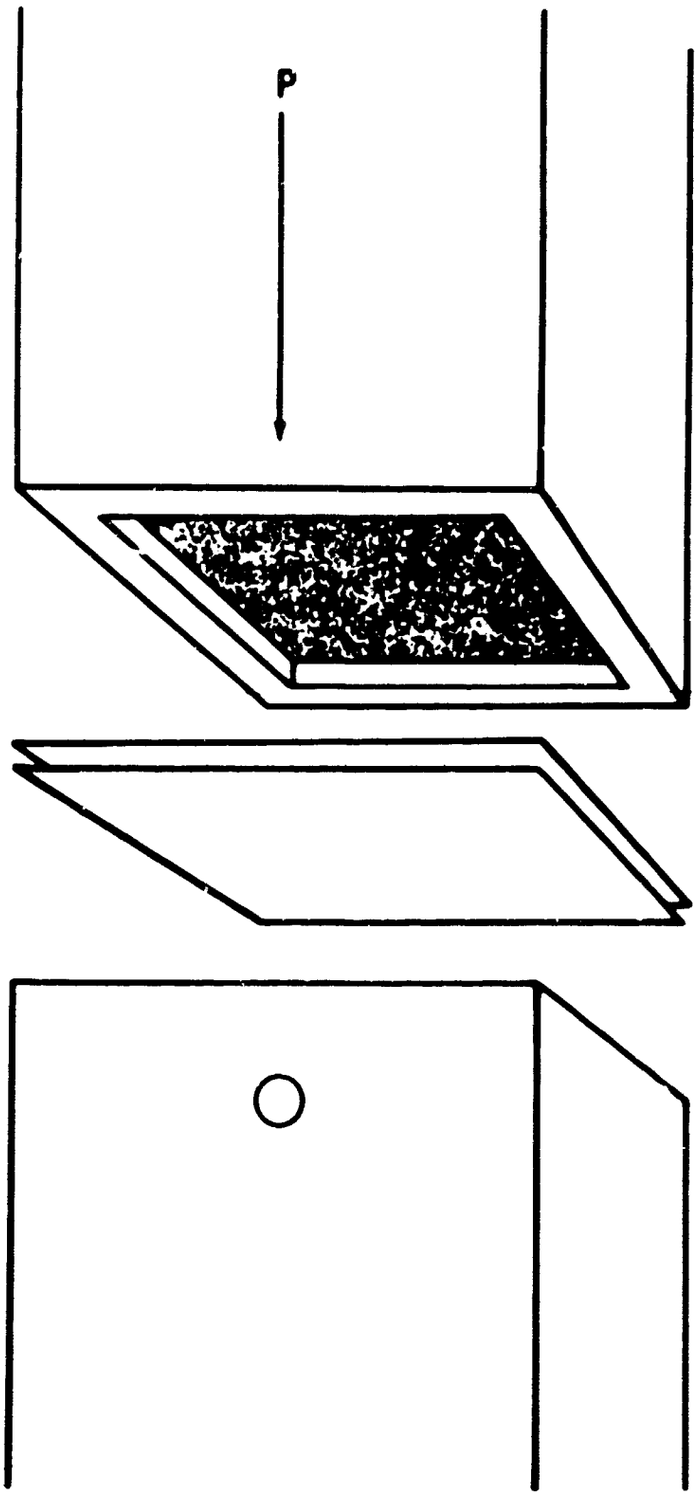


FIGURE 6 Setup for sealing sample edges by Hot Press Bonding
(Induction Heating Coil is not Shown)

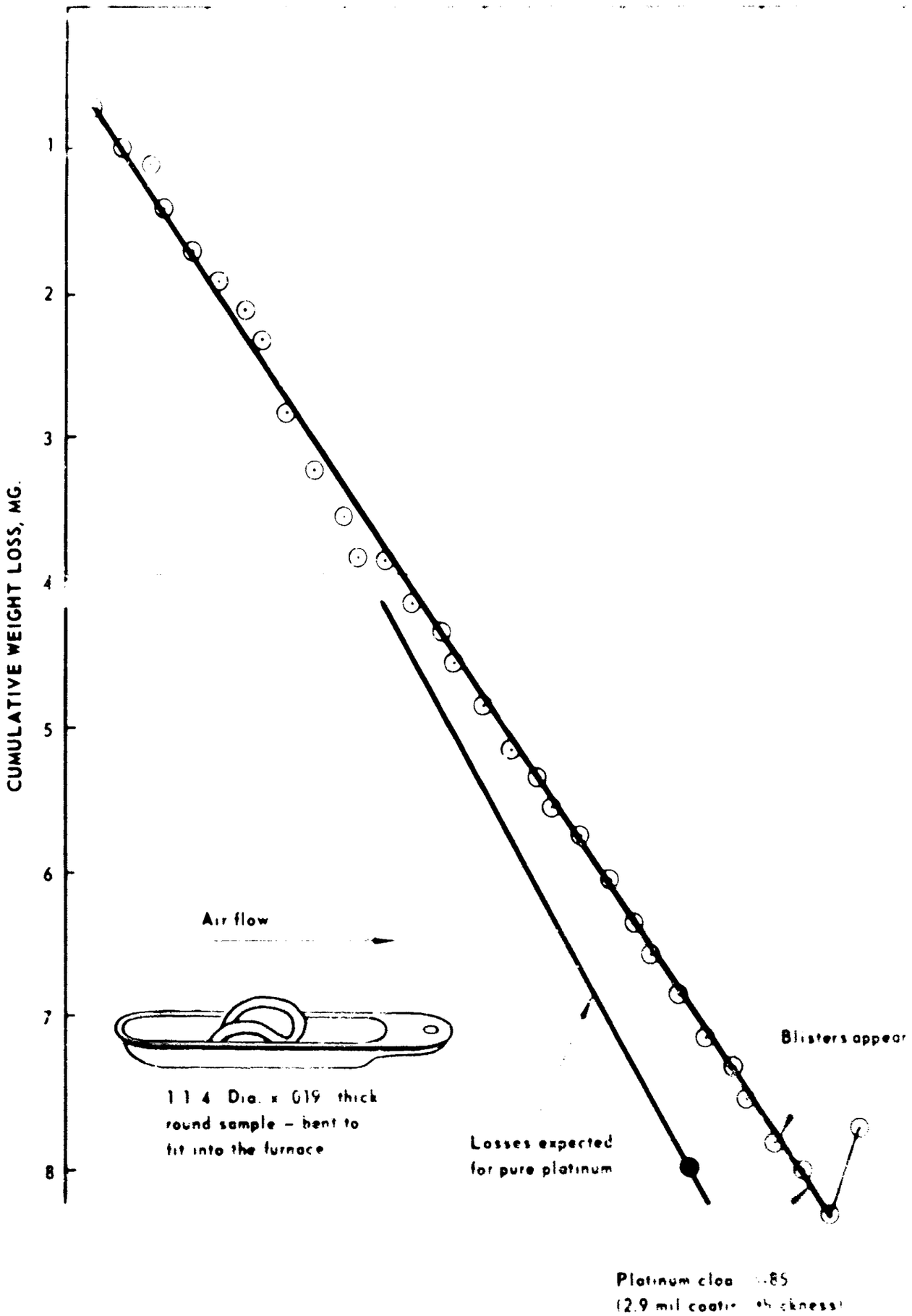


FIGURE 7 Weight Losses for Platinum Clad FS-85 at 2200 F in a 24 cpm Air Flow

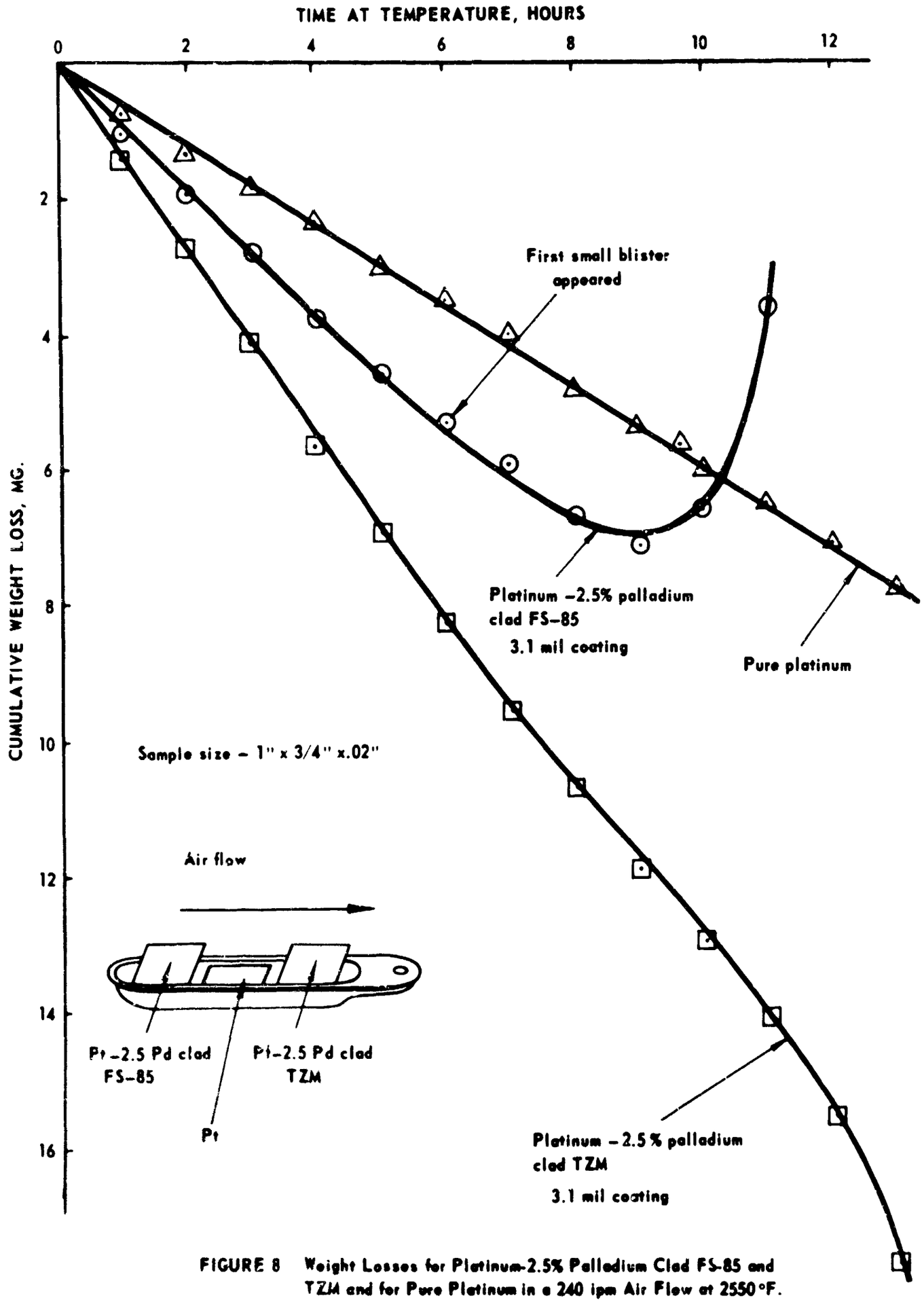


FIGURE 8 Weight Losses for Platinum-2.5% Palladium Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Air Flow at 2550°F.

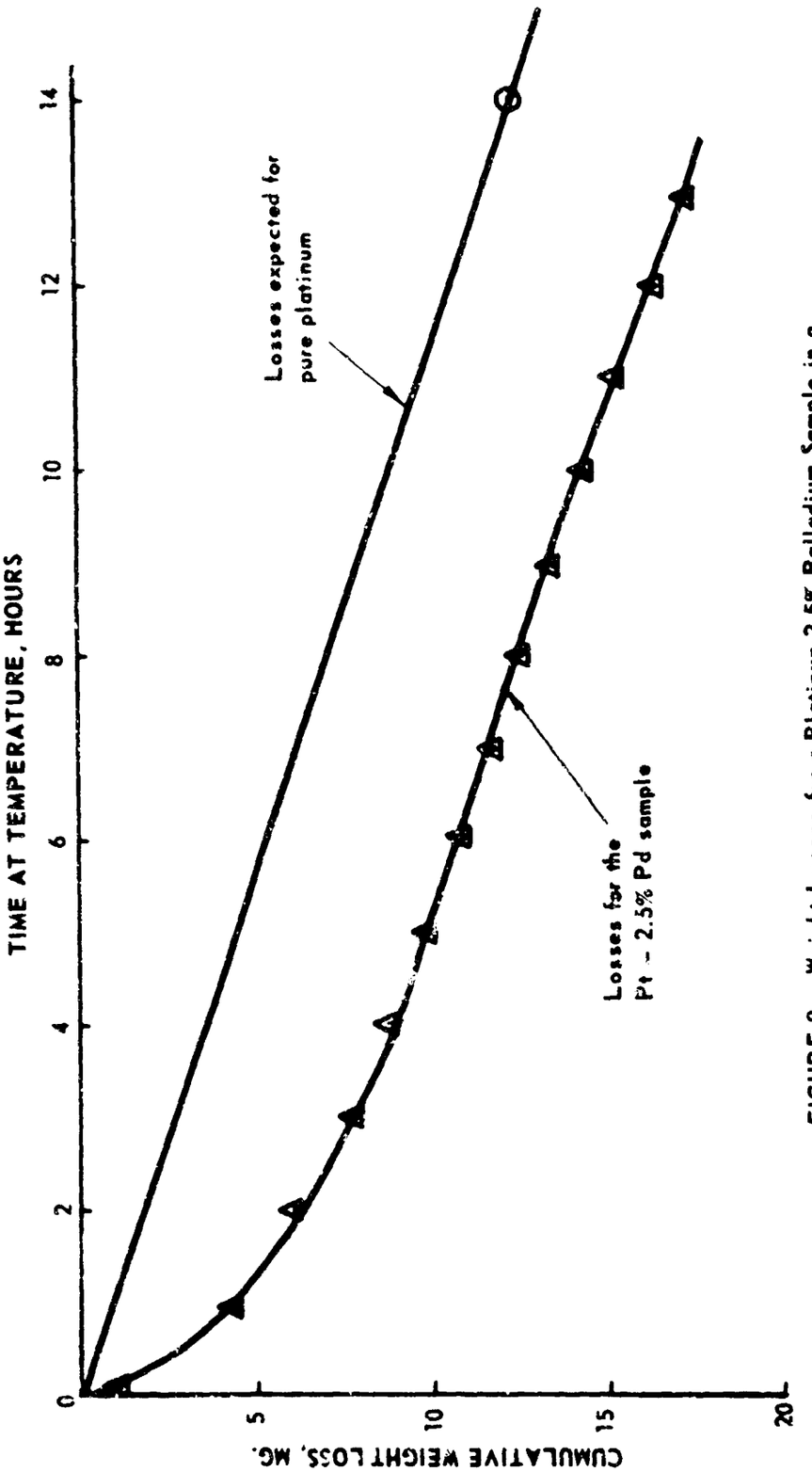


FIGURE 9 Weight Losses for a Platinum-2.5% Palladium Sample in a 240 ipm Air Flow at 2550°F.

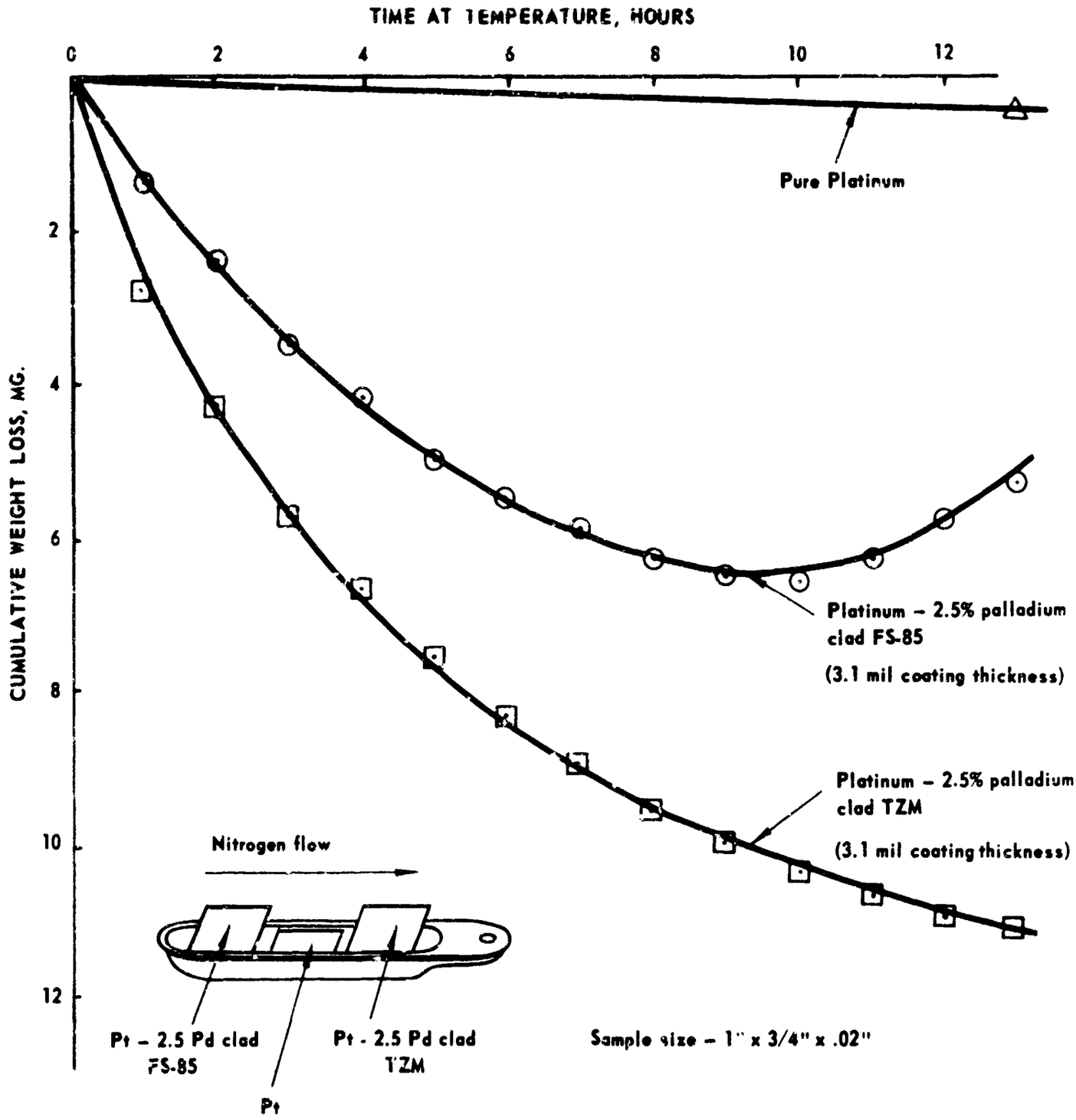


FIGURE 10 Weight Losses for Platinum-2.5% Palladium Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Nitrogen Flow at 2550°F.

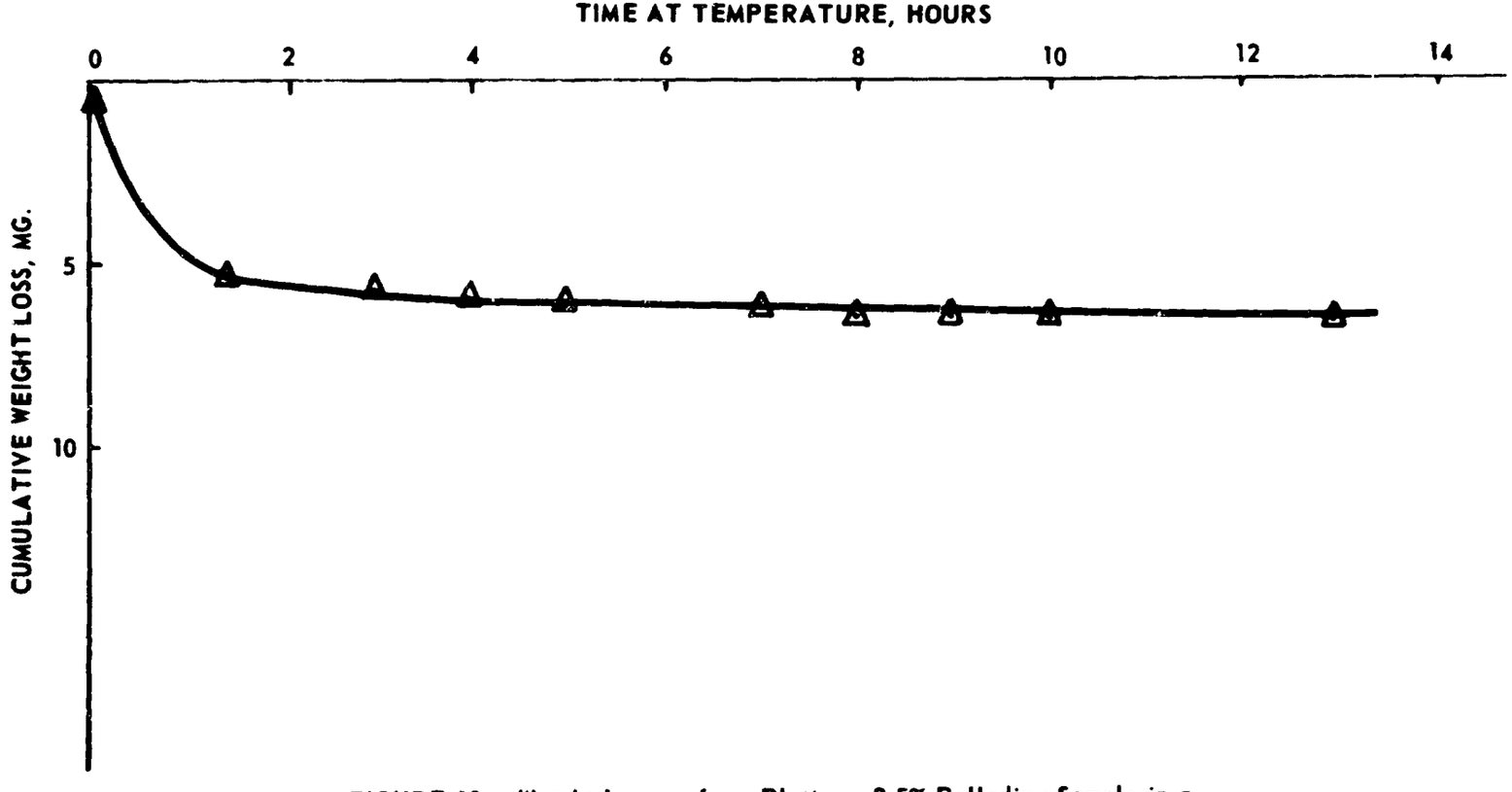
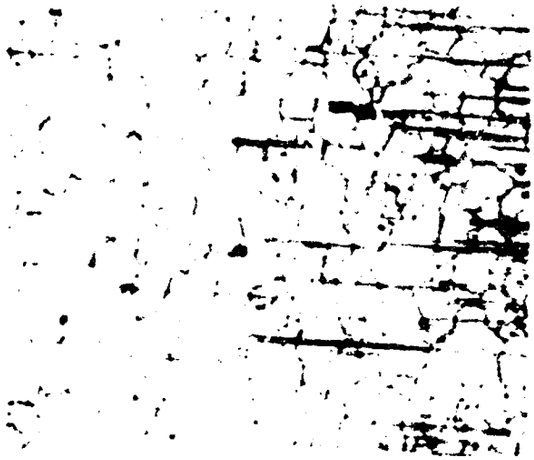


FIGURE 11 Weight Losses for a Platinum-2.5% Palladium Sample in a 240 ipm Nitrogen Flow at 2550°F.



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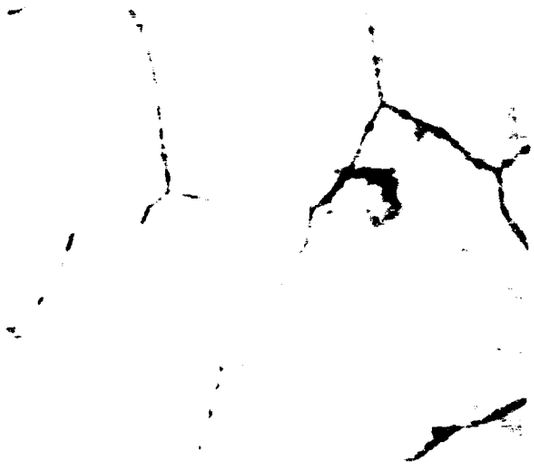
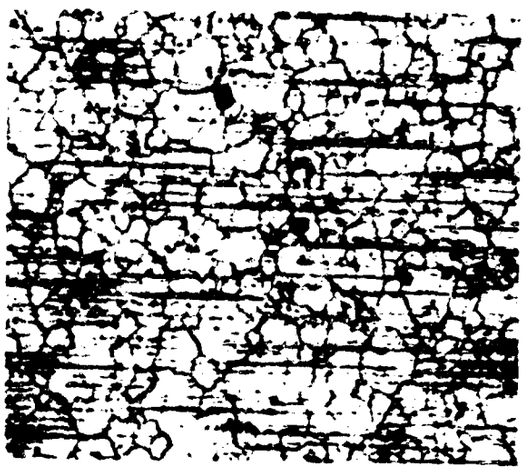


1000X

FIGURE 12

Surface Condition of a Platinum-2.5% Palladium Clad FS-85 Sample After One Hour of Testing at 2550 F in a 240 ipm Air Flow



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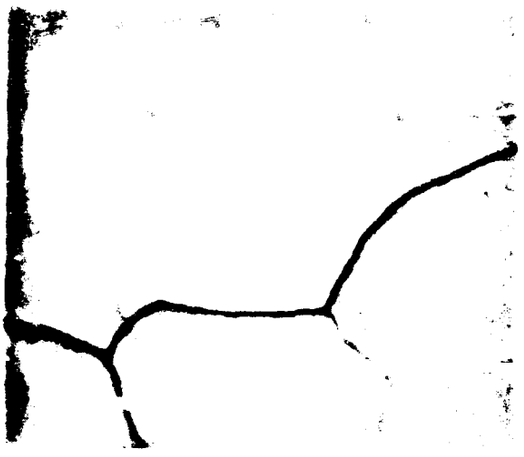
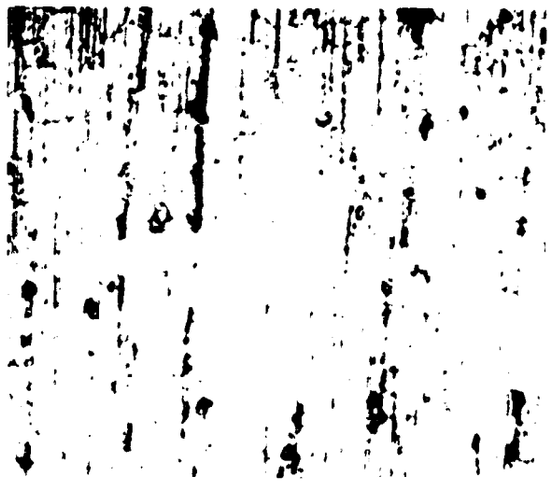


FIGURE 13

Surface Condition of a Platinum-2.5% Palladium Clad TZM Sample After One Hour of Testing at 2550°F in a 240 ipm Air Flow



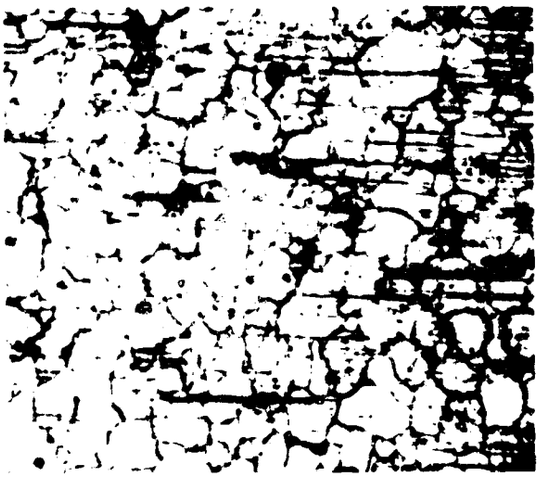
60X

400X

1000X

FIGURE 14

Surface Condition of a Platinum-2.5% Palladium Sample After One Hour of Testing at 2550°F in a 240 ipm Air Flow



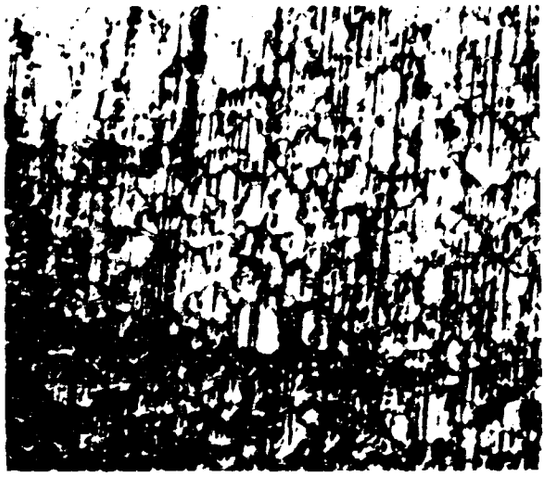
60X

400X

1000X

FIGURE 15

Surface Condition of the Platinum-2 5% Palladium Clad FS-85 Sample After Testing to Coating Failure (Seven Hours) at 2550 F in a 240 ipm Air Flow



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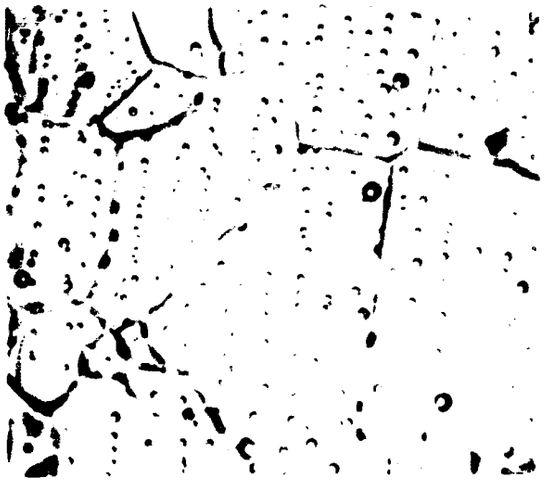
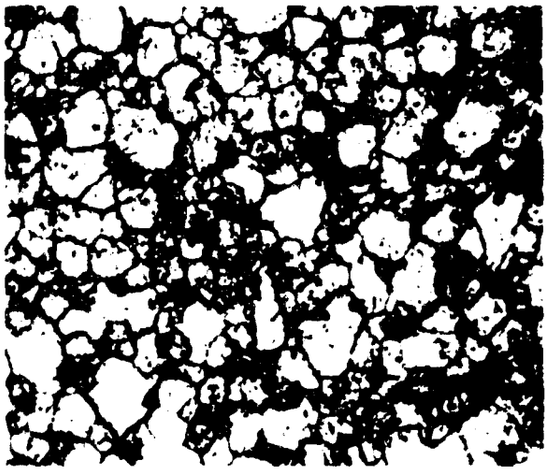


400X

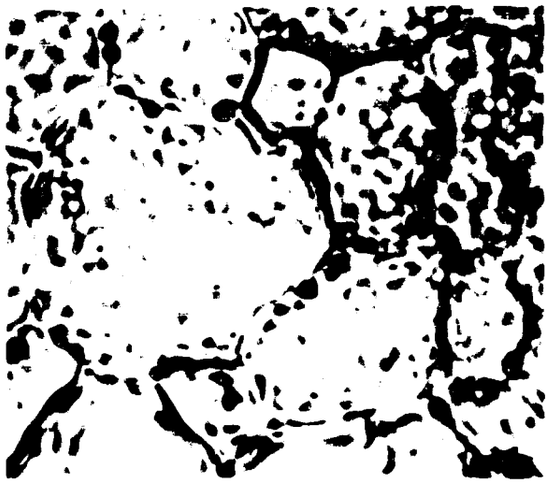
1000X

FIGURE 16

Surface Condition of the Platinum-2.5% Palladium Sample After Testing Seven Hours at 2550 F in a 240 ipm Air Flow



60X

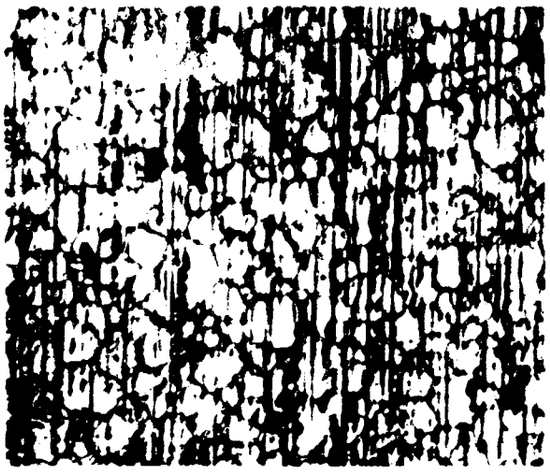


400X

1000X

FIGURE 17

Surface Condition of the Platinum-2.5% Palladium Clad TZM Sample After Testing to Coating Failure (Thirteen Hours) at 2550 F in a 240 ipm Air Flow



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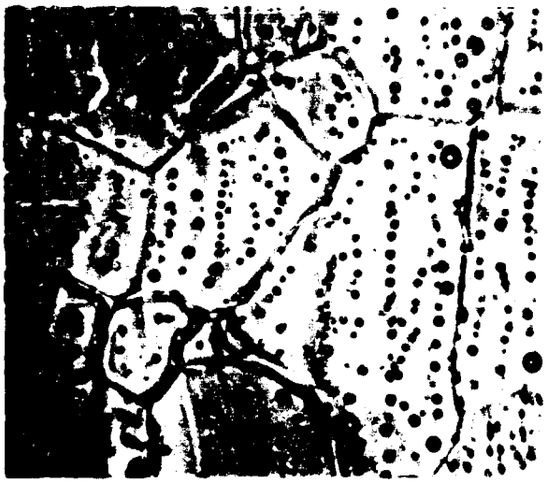

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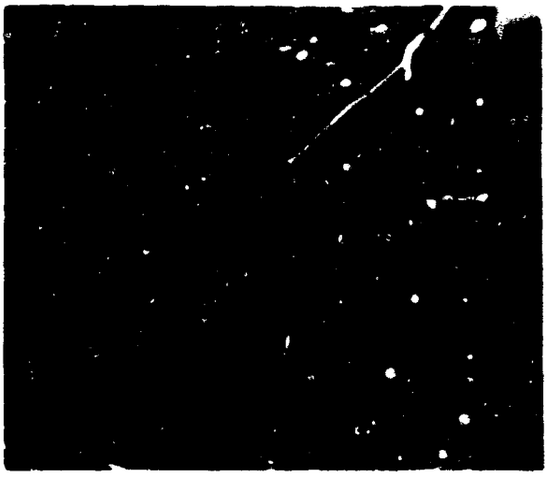

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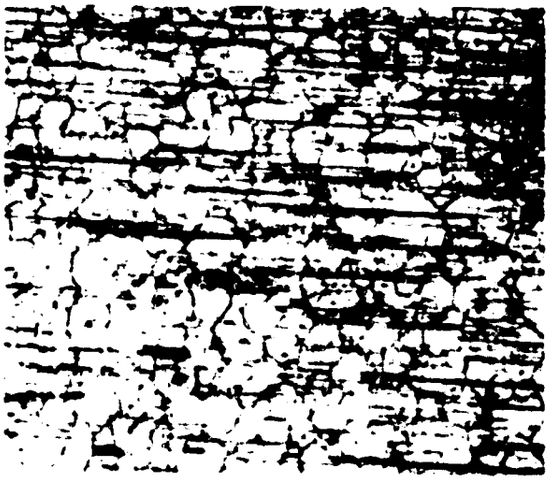
FIGURE 18

Surface Condition of the Platinum-2.5% Palladium Sample After Testing Thirteen Hours at 2550 F in a 240 ipm Air Flow



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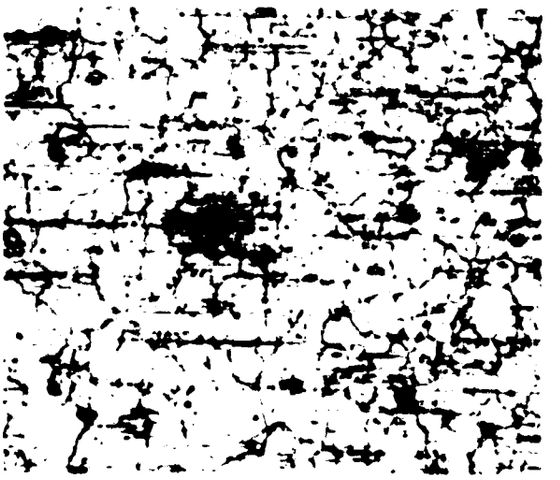

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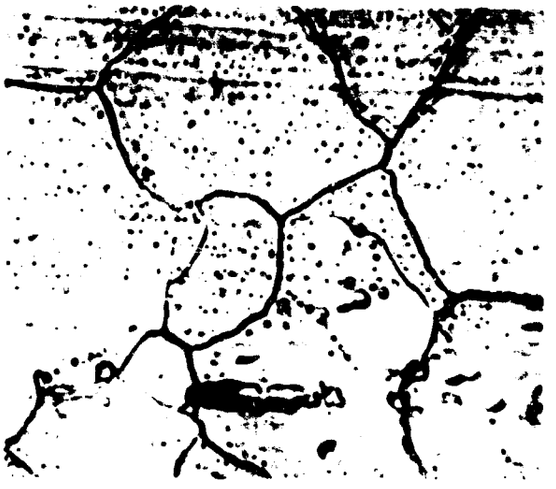


400X

400X

900X

FIGURE 19

Surface Condition of a Platinum-2.5% Palladium Clad FS-85 Sample After One Hour of Testing at 2550 F in a 240 ipm Nitrogen Flow

1000X

FIGURE 20

Surface Condition of a Platinum-2.5% Palladium Clad TZM Sample After One Hour of Testing at 2550 F in a 240 ipm Nitrogen Flow

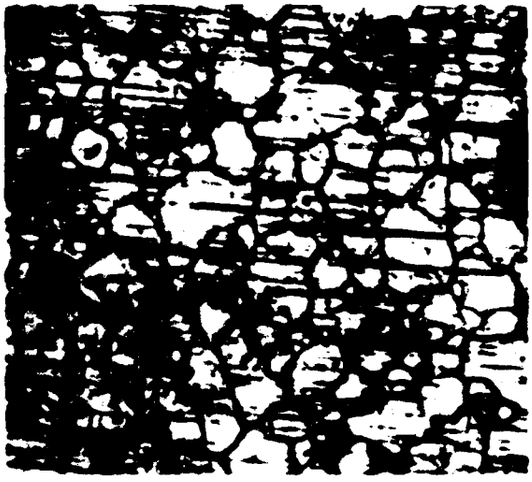
60X

400X

1000X

FIGURE 21

Surface Condition of a Platinum-2 5% Palladium Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow



60X

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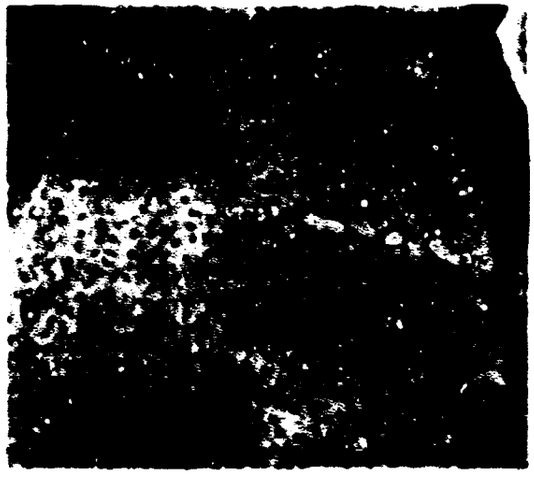


1000X

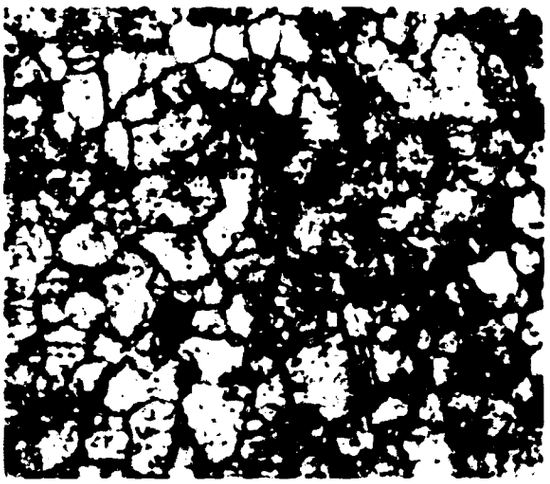
FIGURE 22

Surface Condition of a Platinum-2 5% Palladium Clad FS 85 Sample Tested Seven Hours at 2550 F in a 24 ipm Nitrogen Flow

1000X

FIGURE 23

Surface Condition of a Platinum-2 5% Palladium Sample Tested Seven Hours at 2550 F in a 240 ipm Nitrogen Flow



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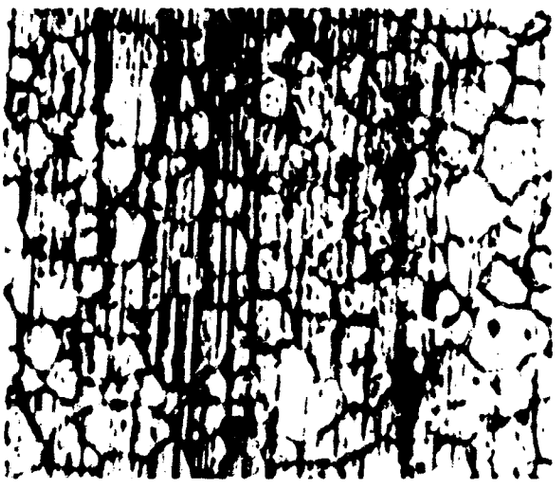

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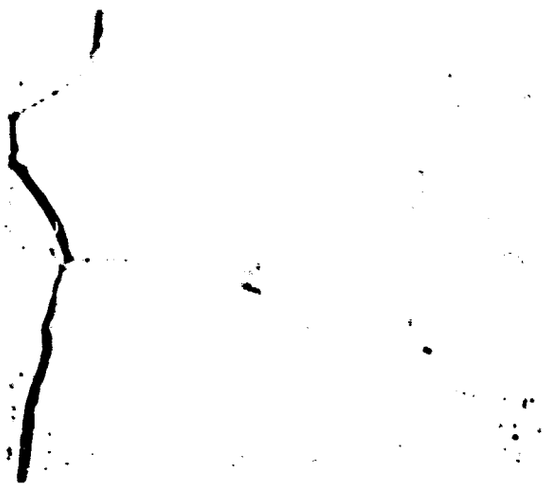


400X

1000X

FIGURE 24

Surface Condition of a Platinum-2.5% Palladium Clad TZM Sample Tested Thirteen Hours at 2550 F in a 240 ipm Nitrogen Flow

1000X

FIGURE 25

Surface Condition of a Platinum-2.5% Palladium Sample Tested Thirteen Hours at 2550 F in a 240 ipm Nitrogen Flow

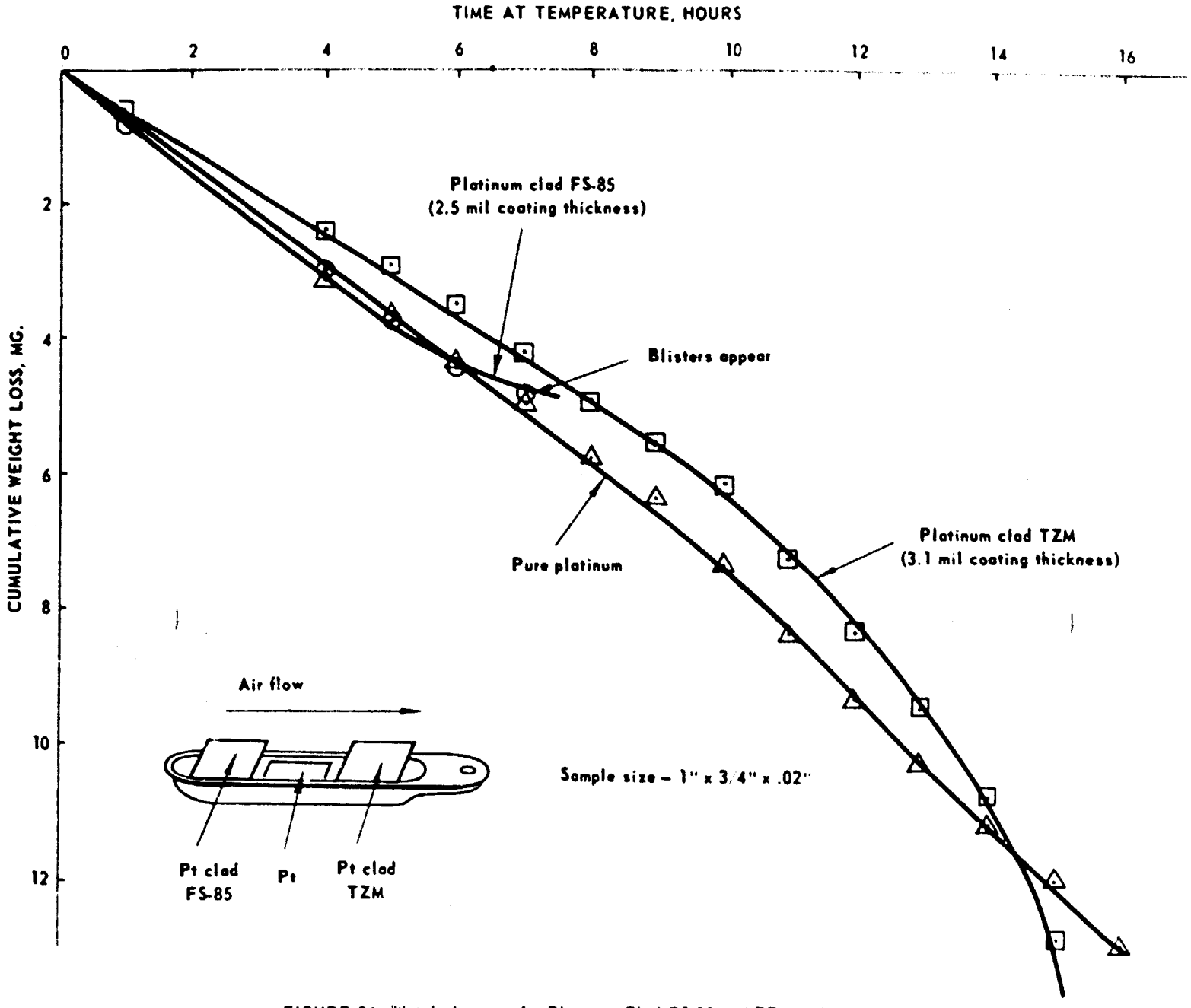


FIGURE 26 Weight Losses for Platinum Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Air Flow at 2550° F.

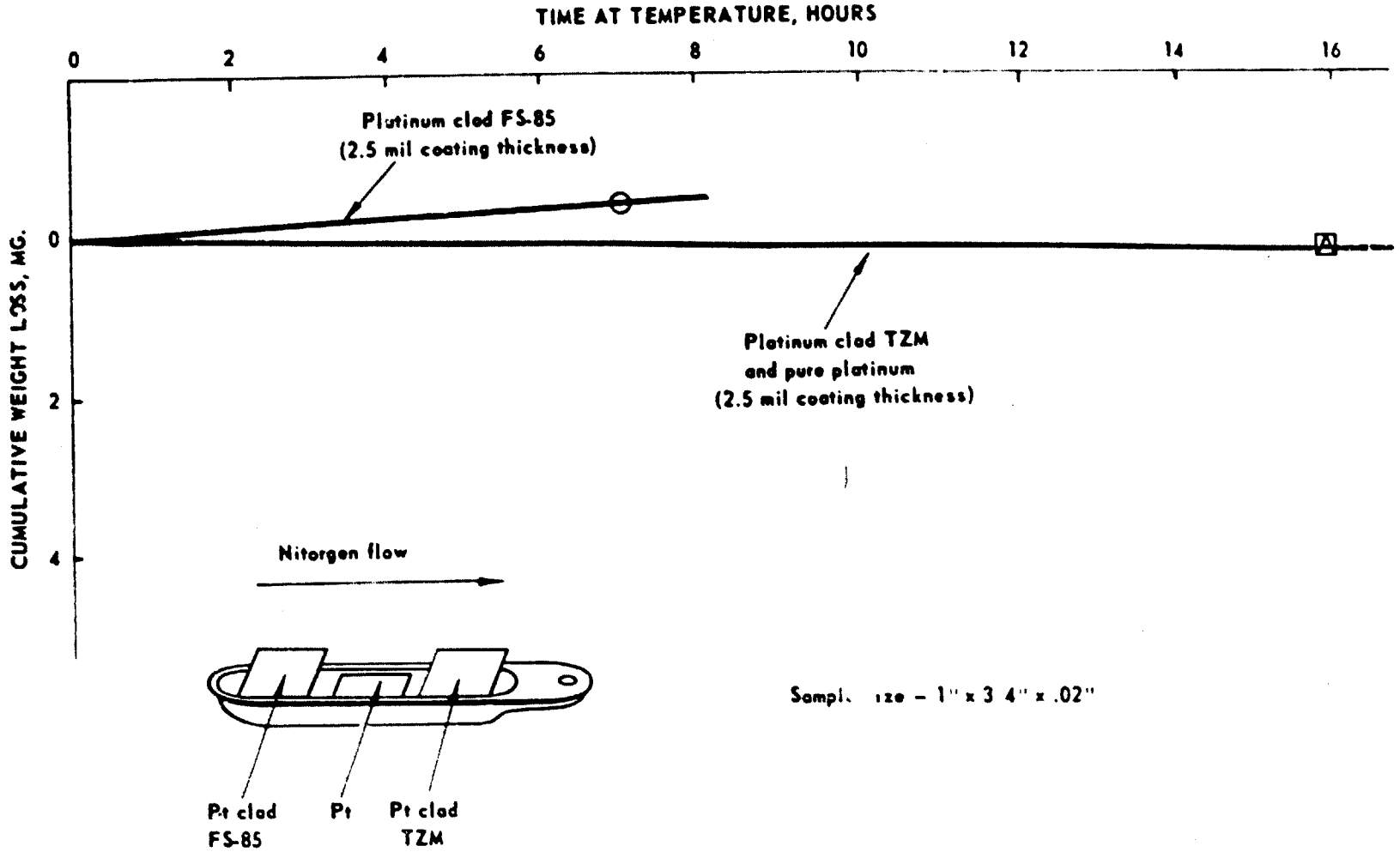
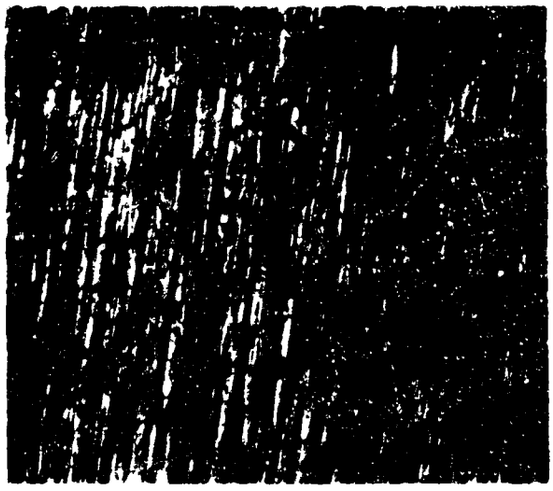


FIGURE 27 Weight Losses for Platinum Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Nitrogen Flow at 2550°F.



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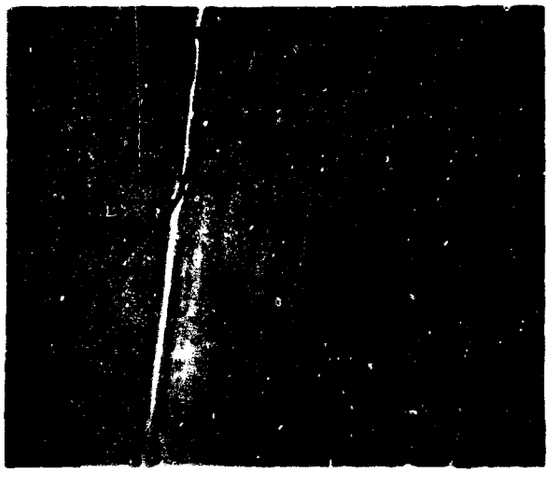
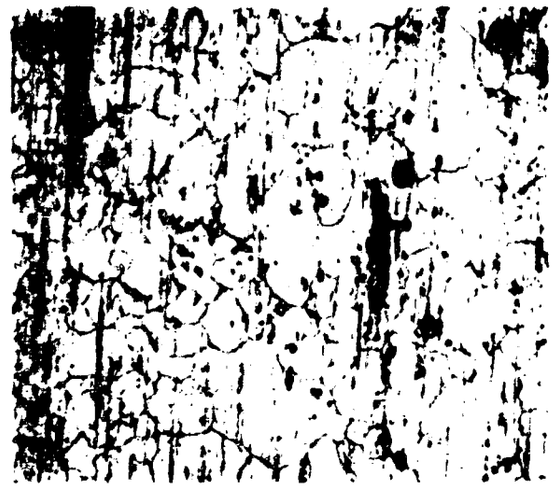
400X



1000X

FIGURE 28

Surface Condition of a Platinum Clad FS-85 Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow



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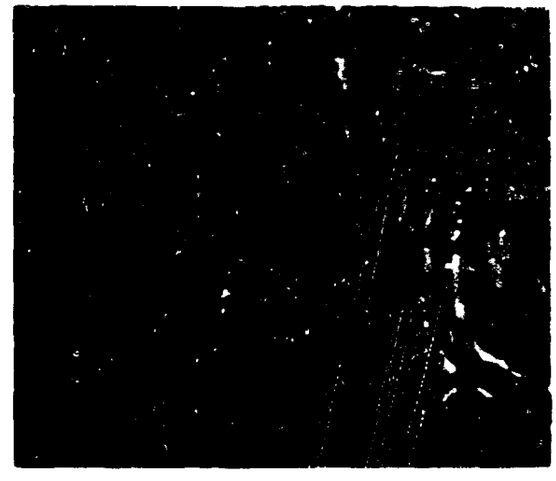
400X

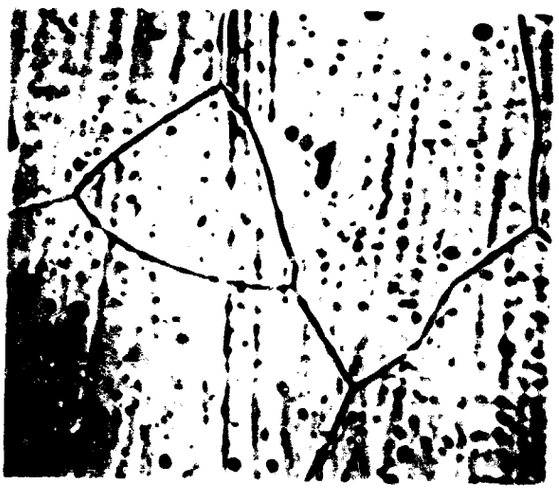


1000X

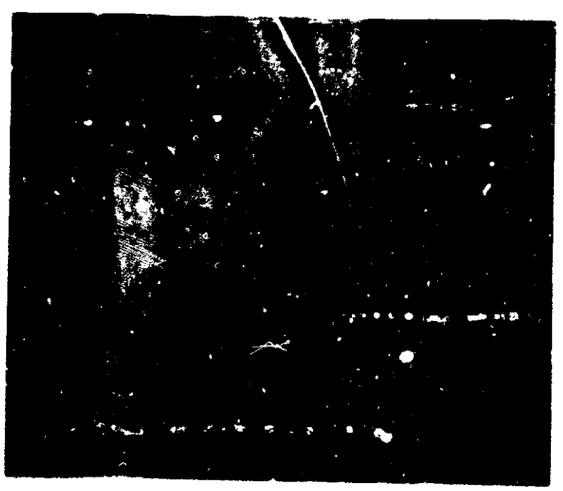
FIGURE 29

Surface Condition of a Platinum Clad TZM Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow

60X

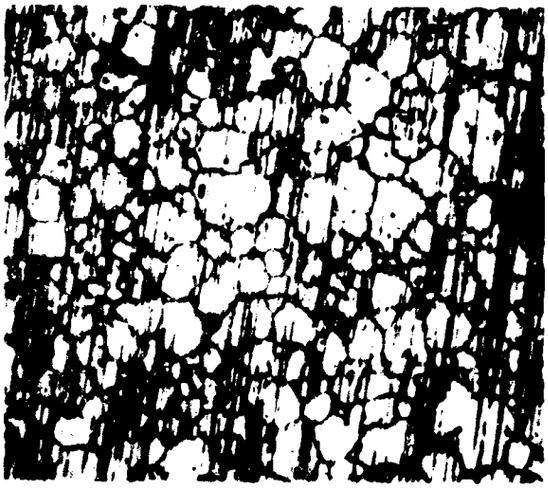


400X



1000X

FIGURE 30
Surface Condition of a Platinum Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow



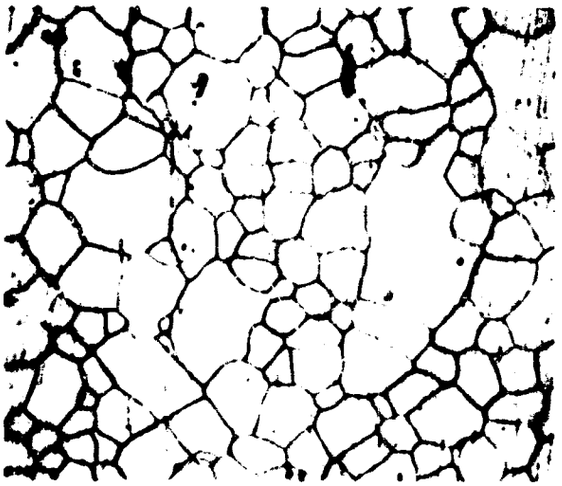
60X

400X

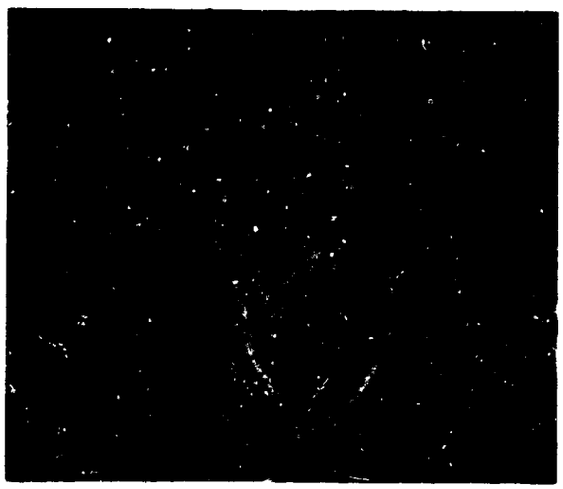
1000X

FIGURE 31

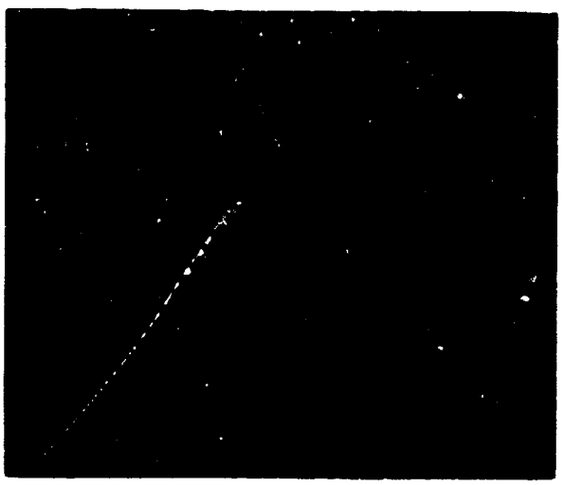
Surface Condition of the Platinum-clad FS-85 Sample After Testing to Coating Failure (Seven Hours) at 2550 F in a 240 ipm Air Flow



60X



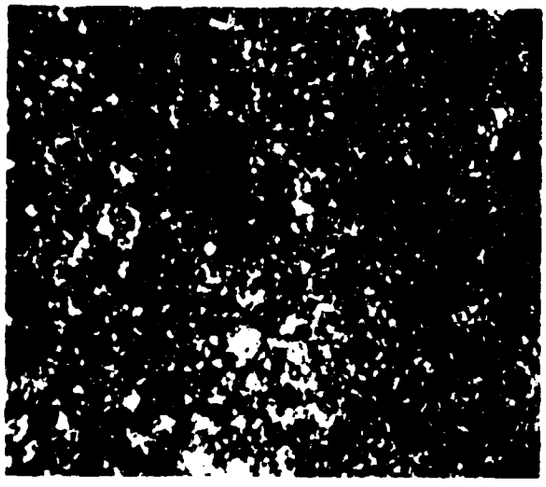
400X



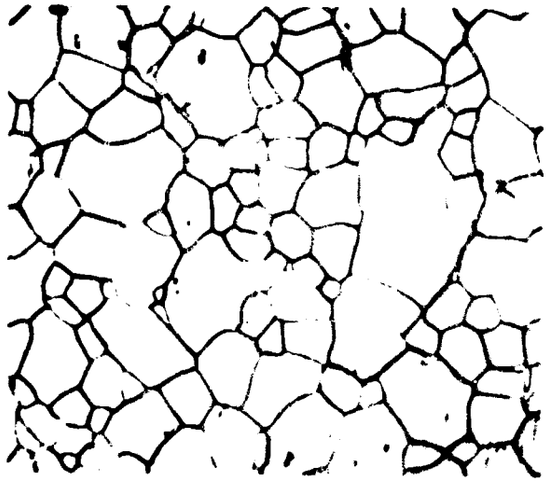
1000X

FIGURE 32

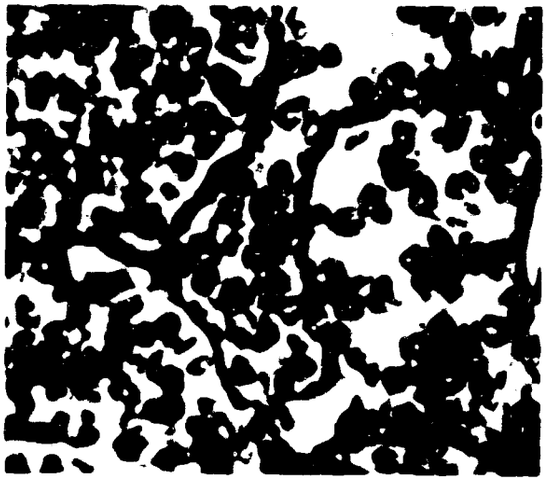
Surface Condition of the Platinum Sample After Testing Seven Hours at 2550 F in a 240 ipm Air Flow



60X

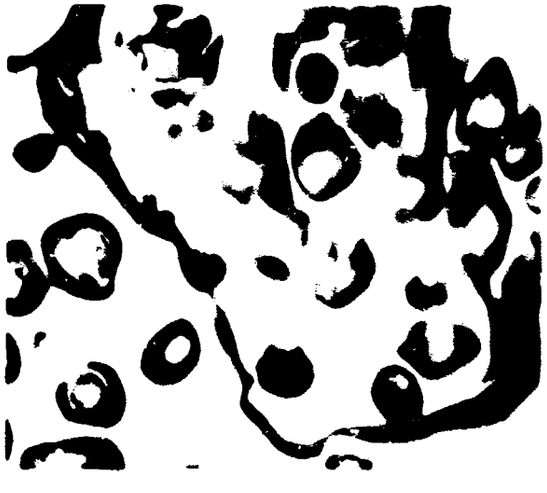


60X

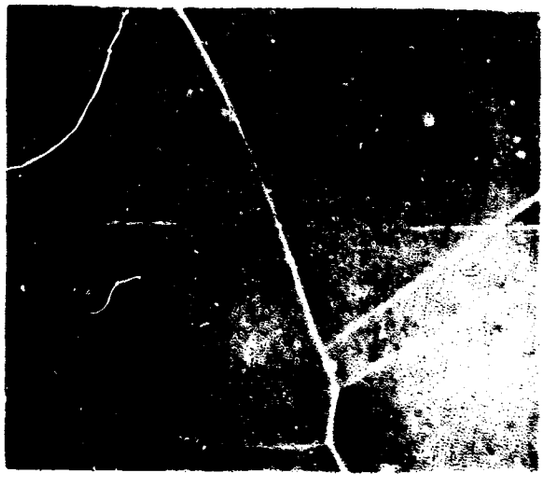


400X

400X



1000X



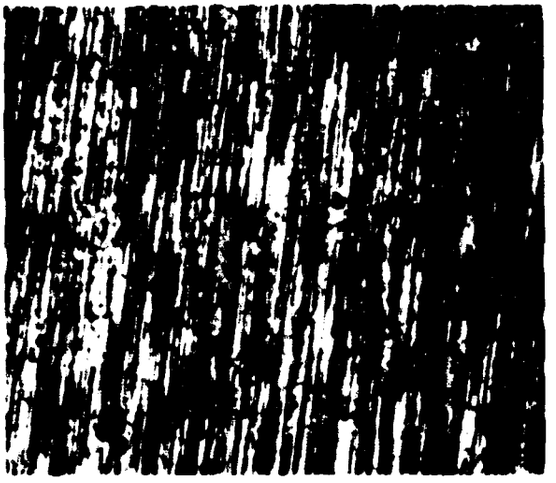
1000X

FIGURE 33

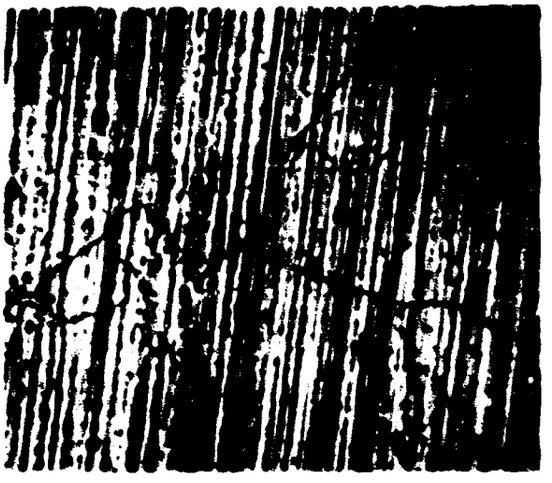
Surface Condition of the Platinum Clad TZM Sample After Testing to Coating Failure (16 Hours) at 2550 F in a 240 ipm Air Flow

FIGURE 34

Surface Condition of the Platinum Sample After Testing 16 Hours at 2550 F in a 240 ipm Air Flow



60X



400X

1000X

FIGURE 35

Surface Condition of a Platinum Clad FS-85 Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow

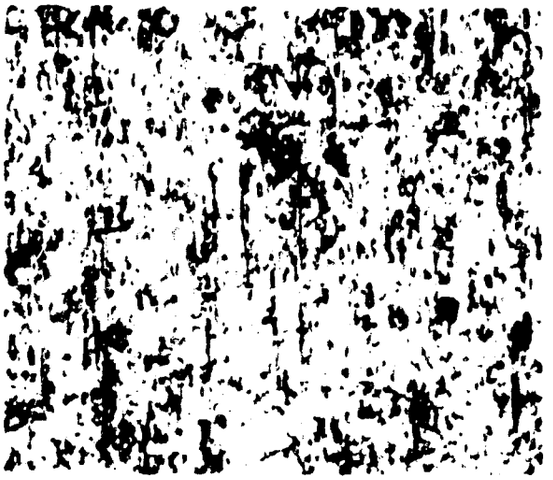
60X

400X

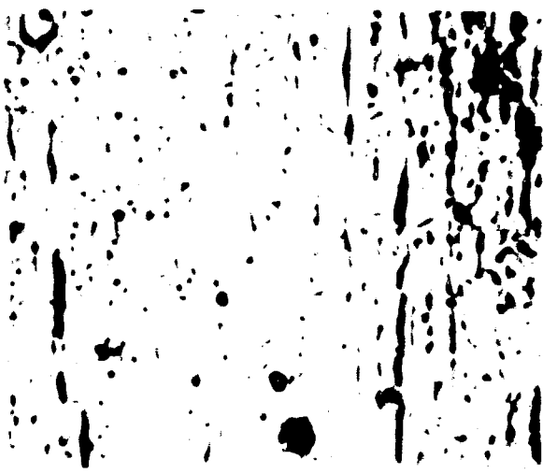
1000X

FIGURE 36

Surface Condition of a Platinum Clad TZM Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow



60X



400X

1000X

FIGURE 37

Surface Condition of a Platinum Sample at the Initiation of Testing at 2550 F in a 240 cpm Nitrogen Flow

60X

60X

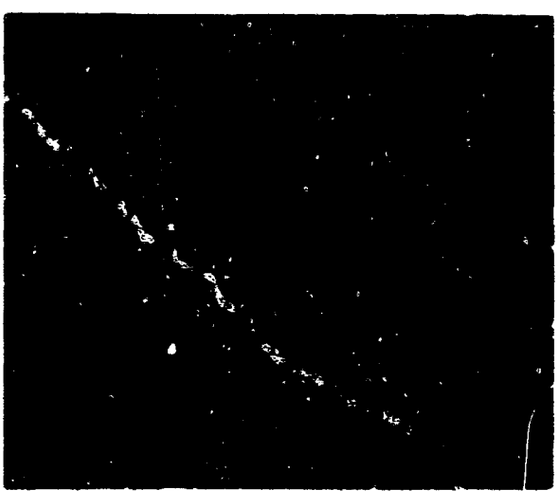
400X

400X

1000X

FIGURE 38

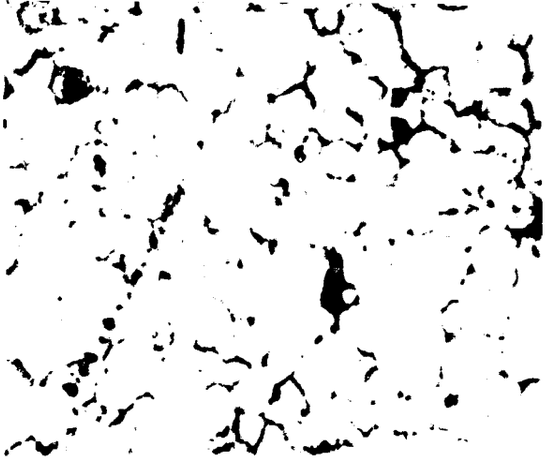
Surface Condition of the Platinum Clad FS-85 Sample Tested Seven Hours at 2550 F in a 240 ipm Nitrogen Flow



1000X

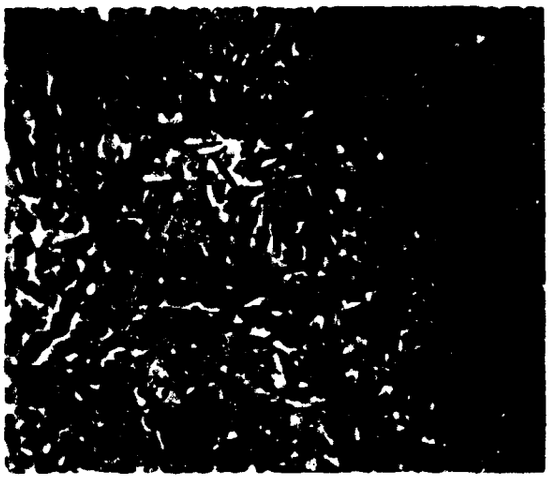
FIGURE 39

Surface Condition of the Platinum Sample Tested Seven Hours at 2550 F in a 240 ipm Nitrogen Flow



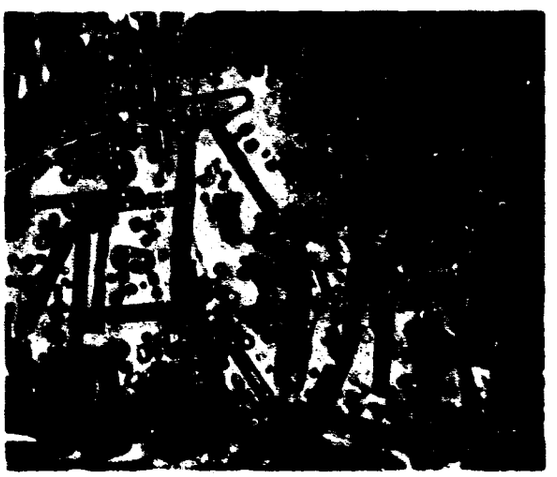
60X

60X



400X

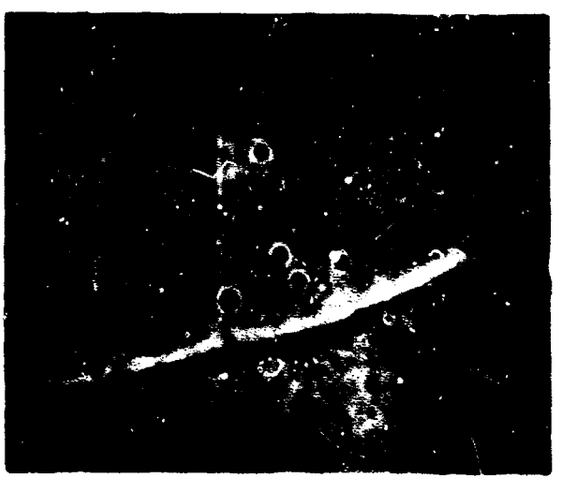
400X



1000X

FIGURE 40

Surface Condition of the Platinum Clad TZM Sample Tested 16 Hours at 2550 F in a 240 cpm Nitrogen Flow



1000X

FIGURE 41

Surface Condition of the Platinum Sample Tested 16 Hours at 2550 F in a 240 cpm Nitrogen Flow

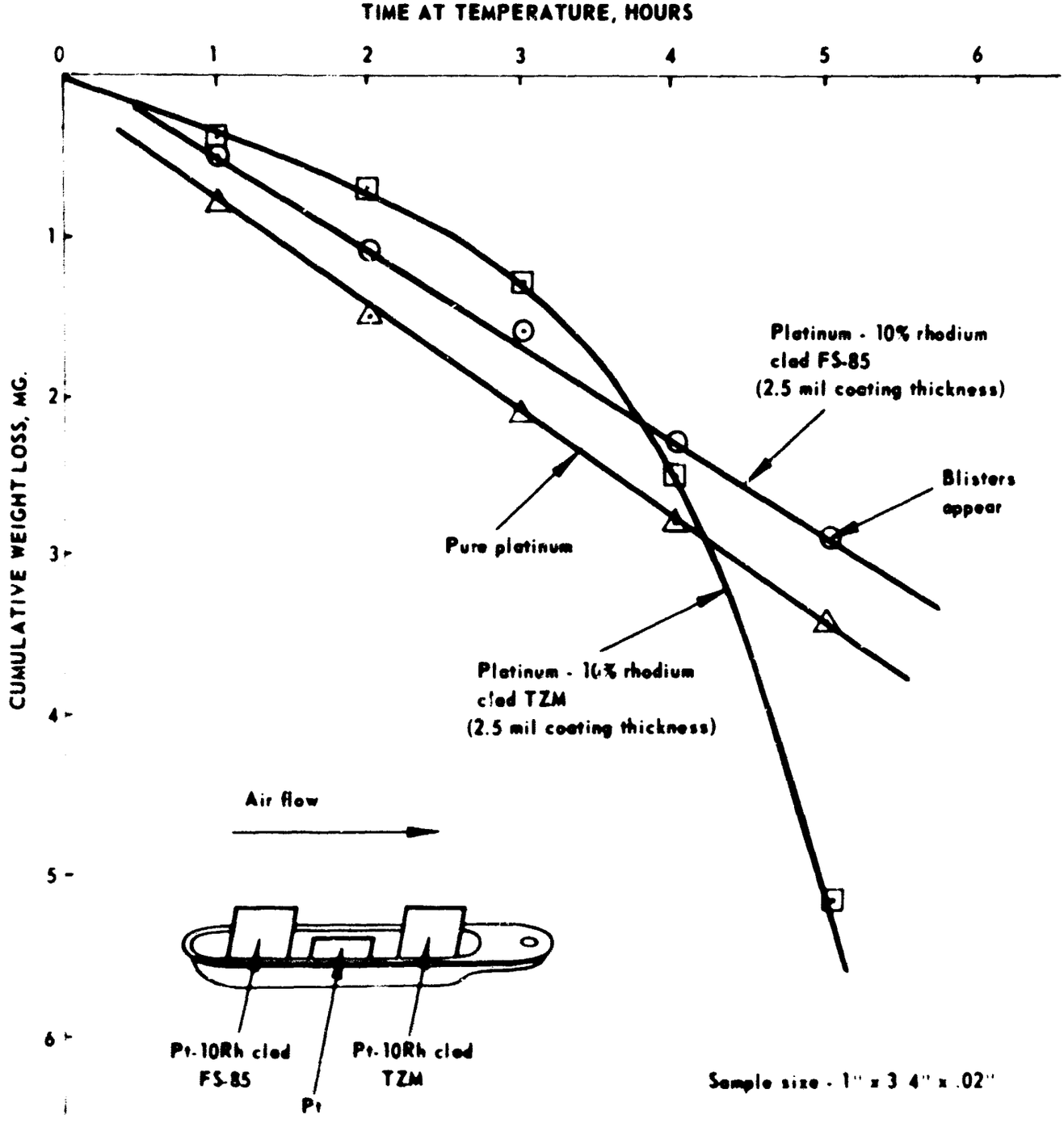


FIGURE 42 Weight Losses for Platinum-10% Rhodium Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Air Flow at 2550 F

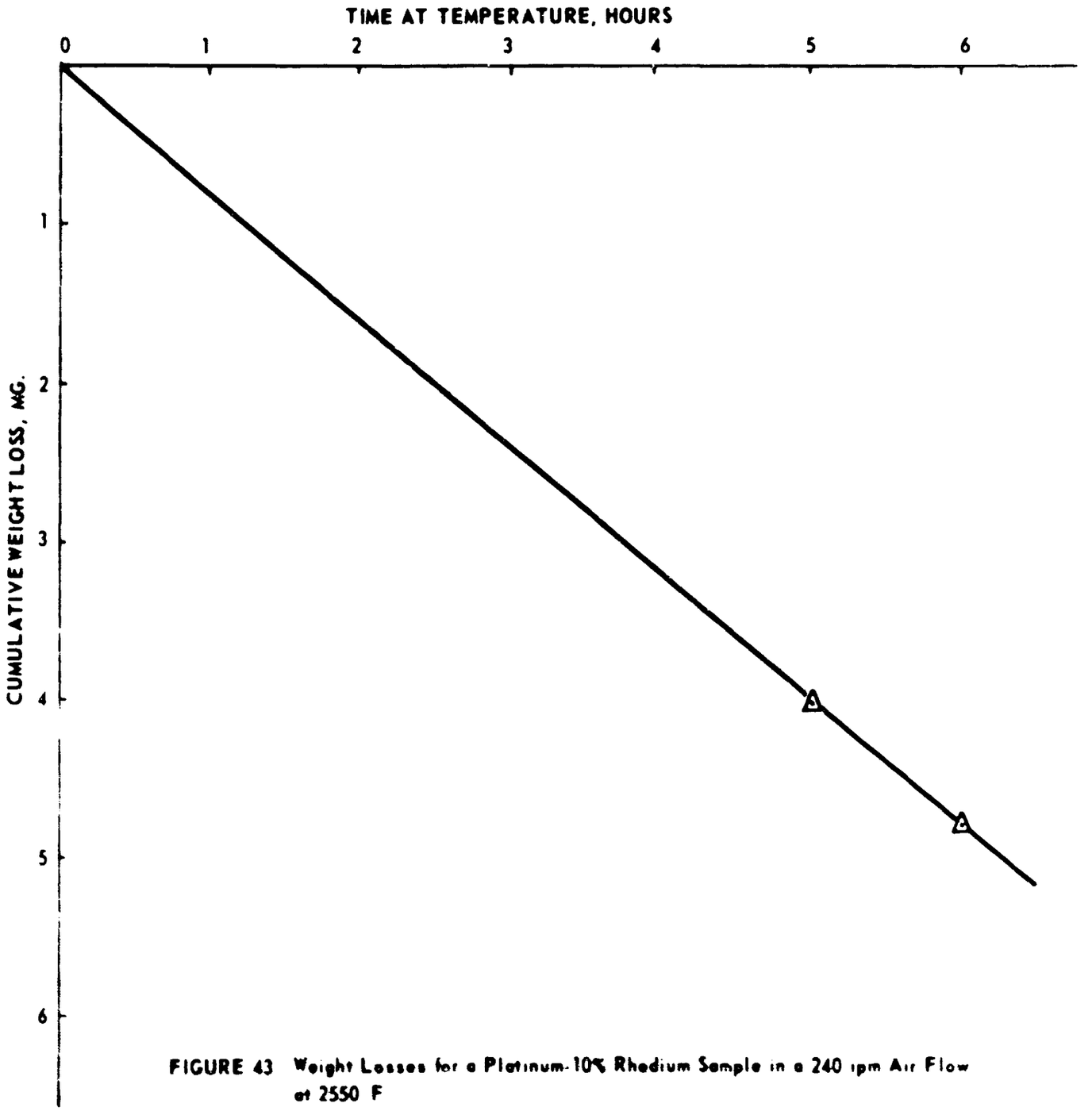


FIGURE 43 Weight Losses for a Platinum-10% Rhodium Sample in a 240 ipm Air Flow at 2550 F

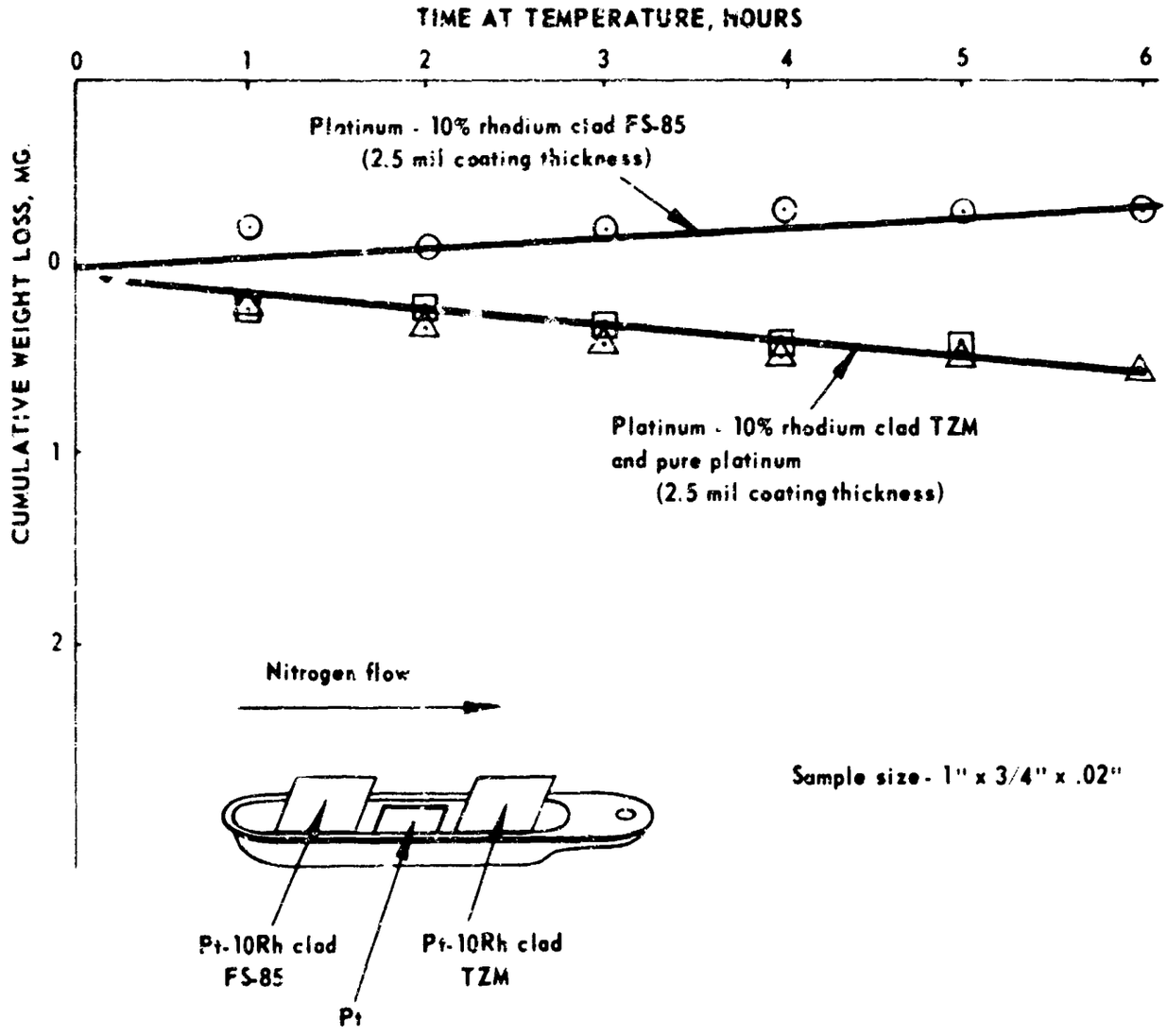


FIGURE 44 Weight Losses for Platinum-10% Rhodium Clad FS-85 and TZM and for Pure Platinum in a 240 ipm Nitrogen Flow at 2550°F.

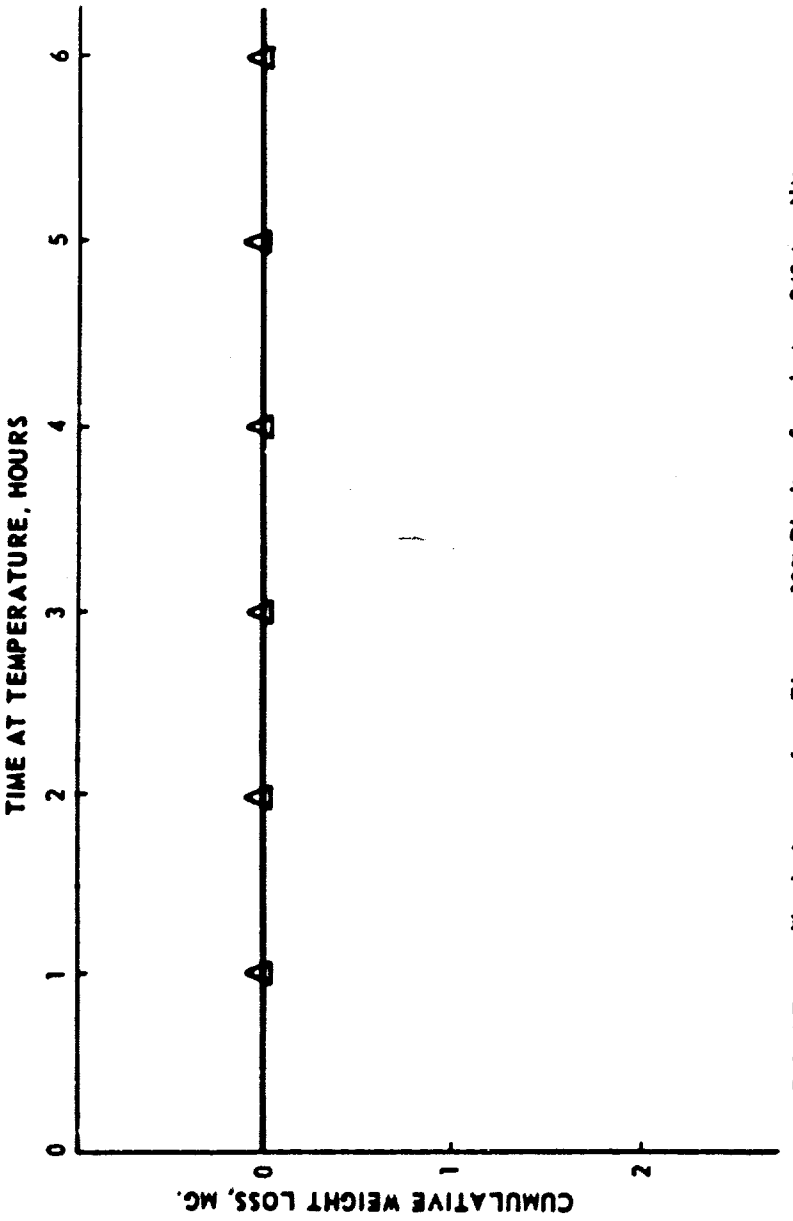
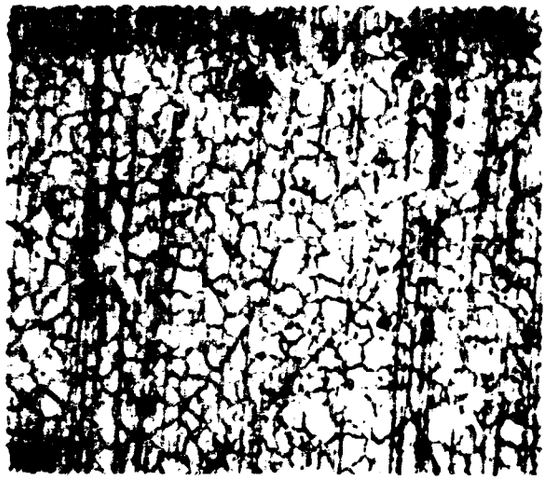
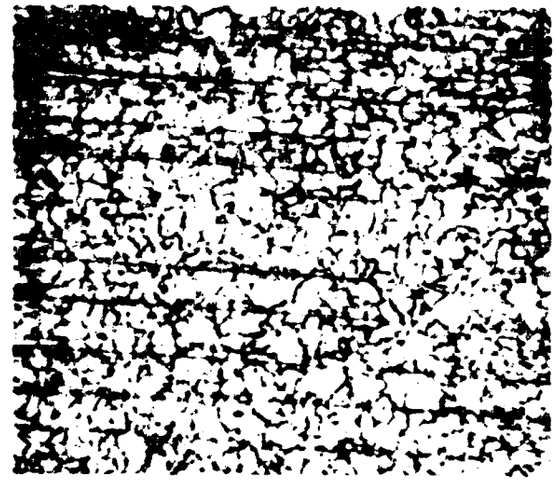


FIGURE 45 Weight Losses for a Platinum-10% Rhodium Sample in a 240 ipm Nitrogen Flow at 2550°F.



60X



60X

400X

400X

1000X

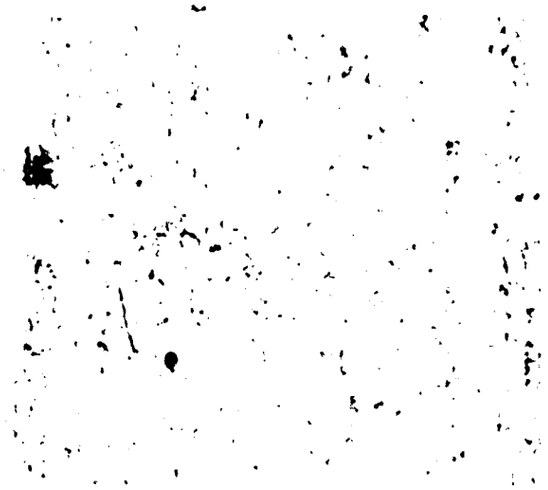
FIGURE 46

Surface Condition of a Platinum-10% Rhodium Clad FS-85 Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow

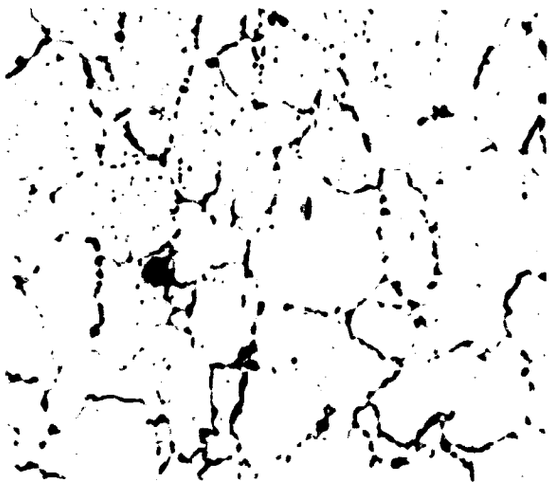
1000X

FIGURE 47

Surface Condition of a Platinum-10% Rhodium Clad TZM Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow



60X

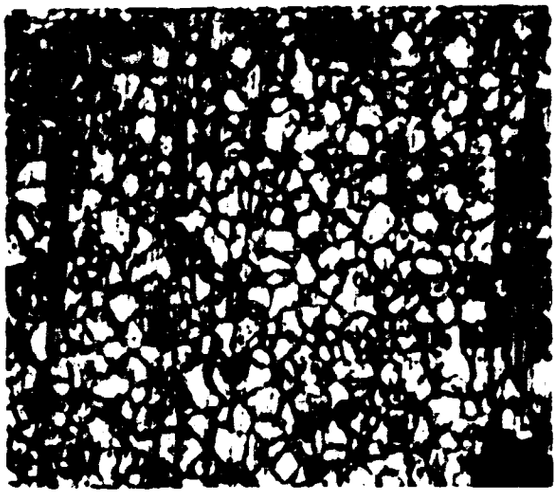


400X

1000X

FIGURE 48

Surface Condition of a Platinum-10% Rhodium Sample at the Initiation of Testing at 2550 F in a 240 ipm Air Flow



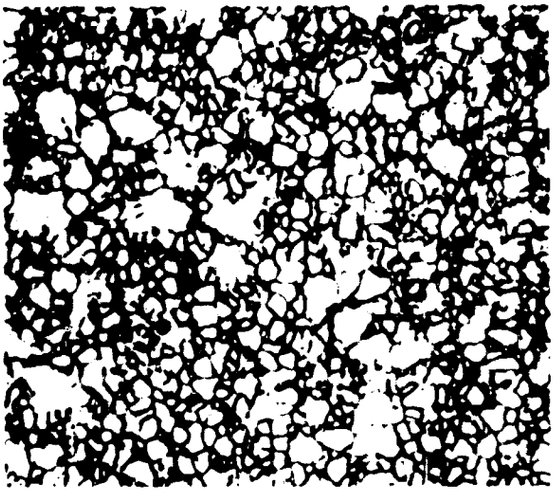
60X

400X

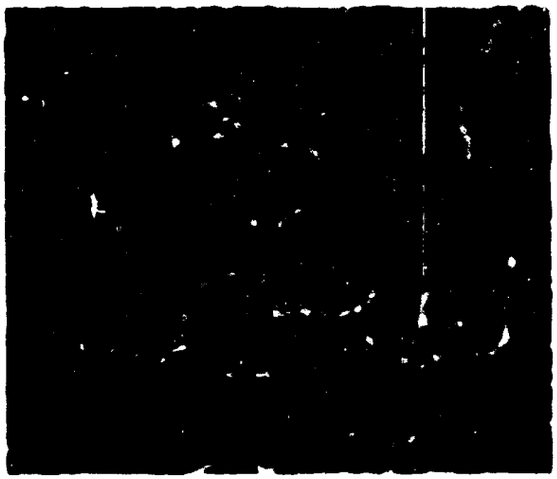
1000X

FIGURE 49

Surface Condition of the Platinum-10% Rhodium Clad FS-85 Sample After Testing to Coating Failure (Six Hours) at 2550 F in a 240 ipm Air Flow



60X

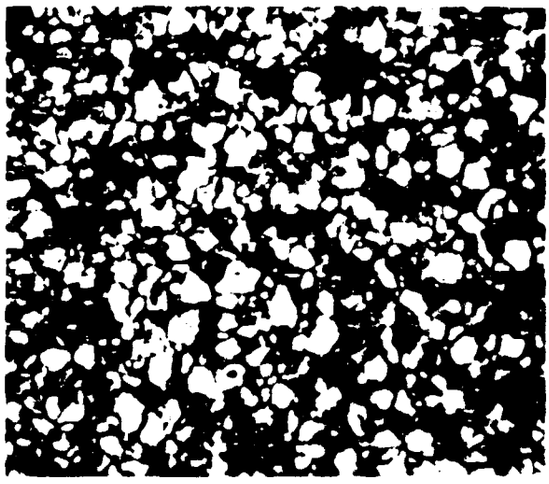


400X

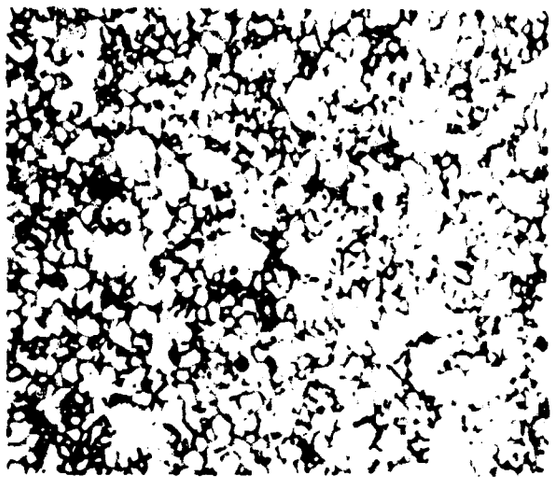
1000X

FIGURE 50

Surface Condition of the Platinum-10% Rhodium Sample After Testing Six Hours at 2550 F in a 240 ipm Air Flow



60X



60X

400X

400X

1000X

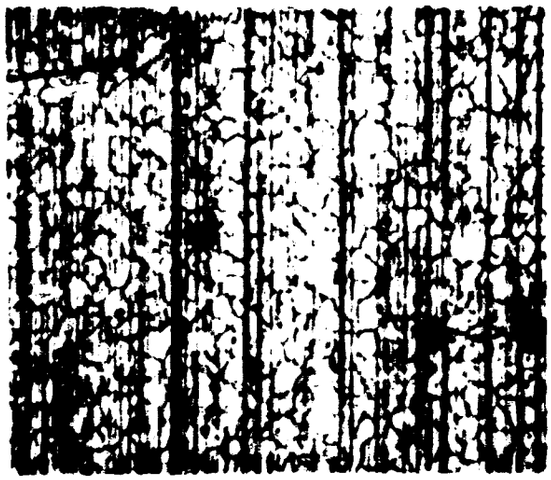
FIGURE 51

Surface Condition of the Platinum-10% Rhodium Clad TZM Sample After Testing to Coating Failure (Five Hours) at 2550 F in a 240 ipm Air Flow

1000X

FIGURE 52

Surface Condition of the Platinum-10% Rhodium After Testing Five Hours at 2550 F in a 240 ipm Air Flow



60X

400X

1000X

FIGURE 53

Surface Condition of a Platinum-10% Rhodium Clad FS-85 Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow

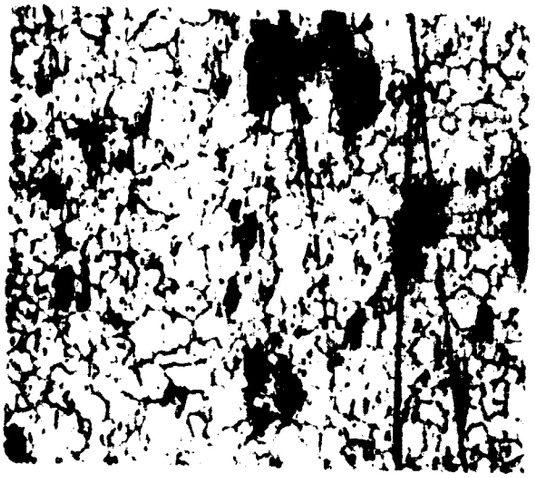
60X

400X

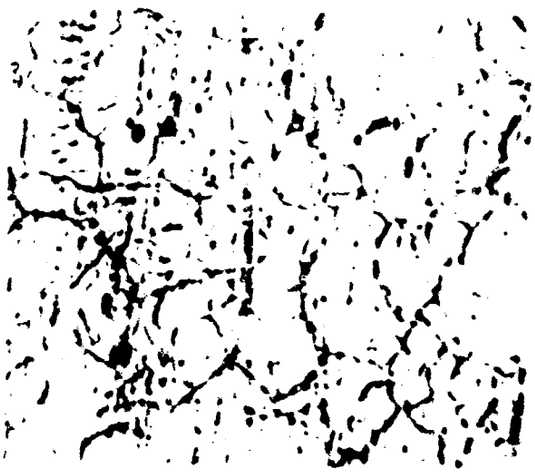
1000X

FIGURE 54

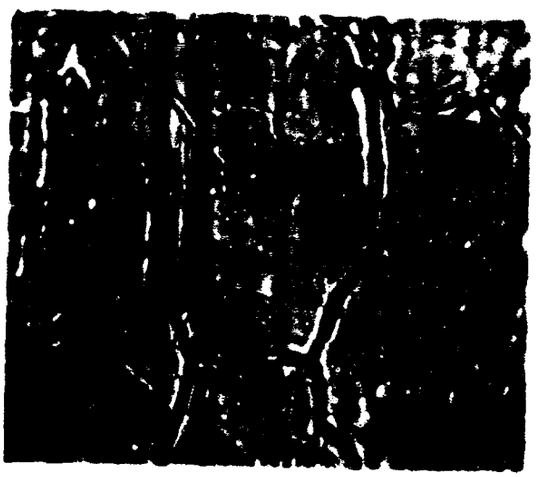
Surface Condition of a Platinum-10% Rhodium Clad TZM Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow



60X



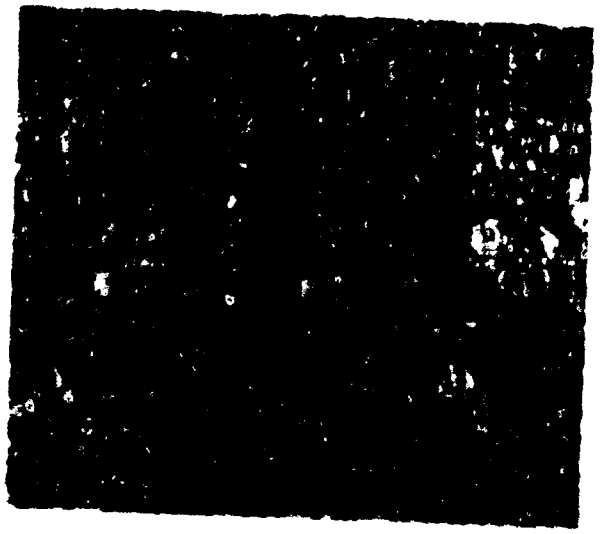
400X



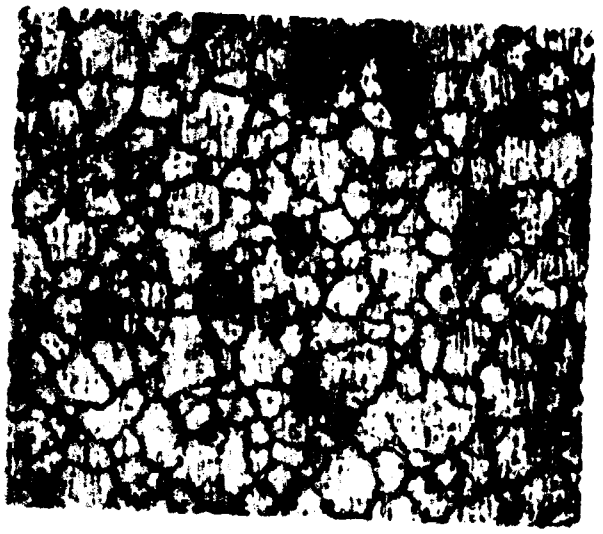
1000X

FIGURE 55

Surface Condition of a Platinum-10% Rhodium Sample at the Initiation of Testing at 2550 F in a 240 ipm Nitrogen Flow



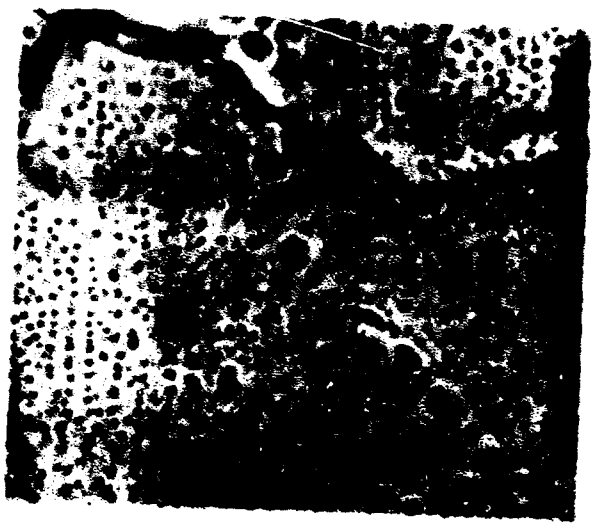
60X



60X

400X

400X



1000X

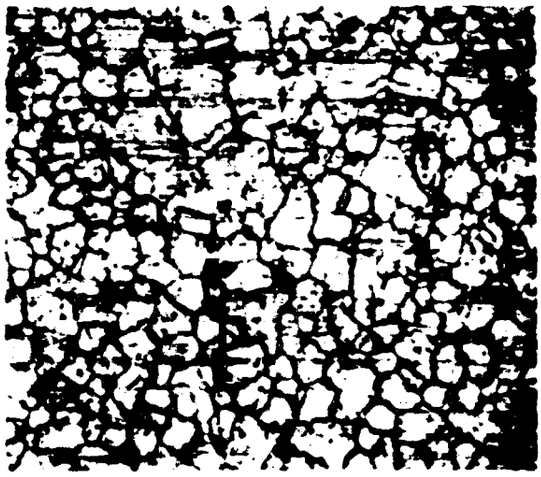
FIGURE 56

Surface Condition of a Platinum-10% Rhodium Clad FS-85 Sample Tested Six Hours at 2550 F in a 240 cpm Nitrogen Flow

1000X

FIGURE 57

Surface Condition of a Platinum-10% Rhodium Sample Tested Six Hours at 2550 F in a 240 cpm Nitrogen Flow



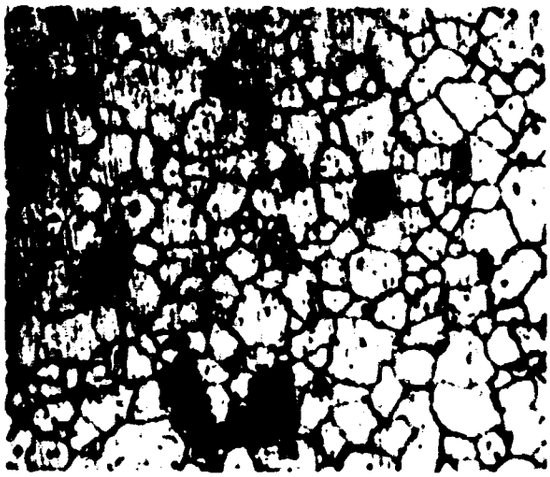
60X

400X

1000X

FIGURE 58

Surface Condition of a Platinum-10% Rhodium Clad TZM Sample Tested Five Hours at 2550 F in a 240 ipm Nitrogen Flow



60X

400X

1000X

FIGURE 59

Surface Condition of a Platinum-10% Rhodium Sample Tested Five Hours at 2550 F in a 240 ipm Nitrogen Flow

600X

1200X

FIGURE 60

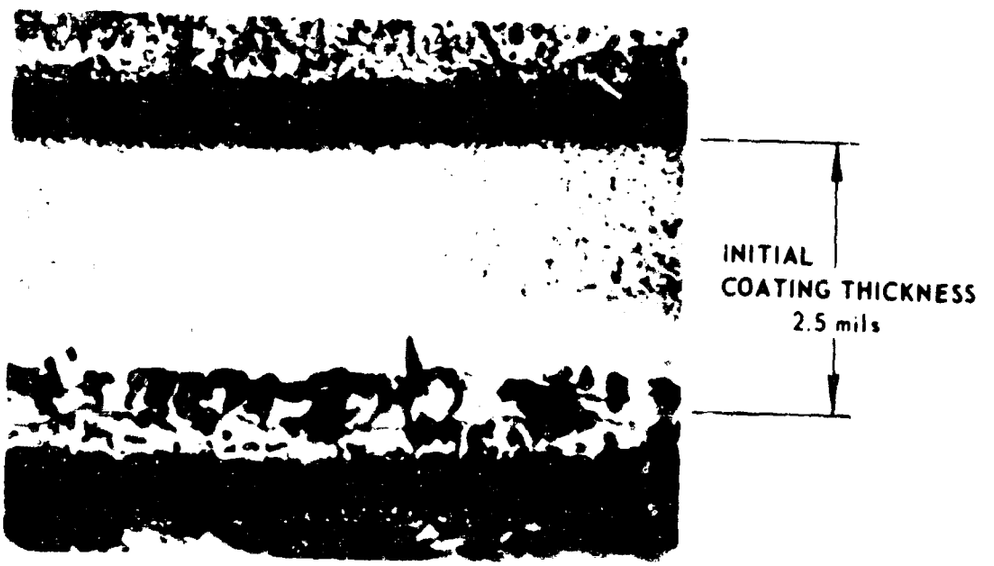
Polished and Etched Cross Section of a Platinum-2.5% Palladium Clad FS-85 After Heating 14 Hours at 2550 F in a 240 cpm Air Flow

450X

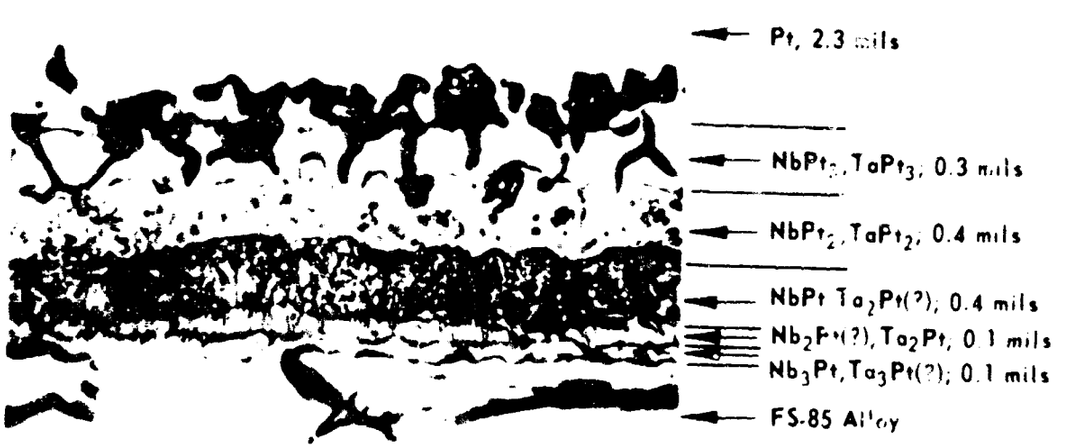
1000X

FIGURE 61

Polished and Etched Cross Section of a Platinum-2 5% Palladium Clad FS-85 Sample After Heating 13 Hours at 2550 F in a 240 ipm Nitrogen Flow



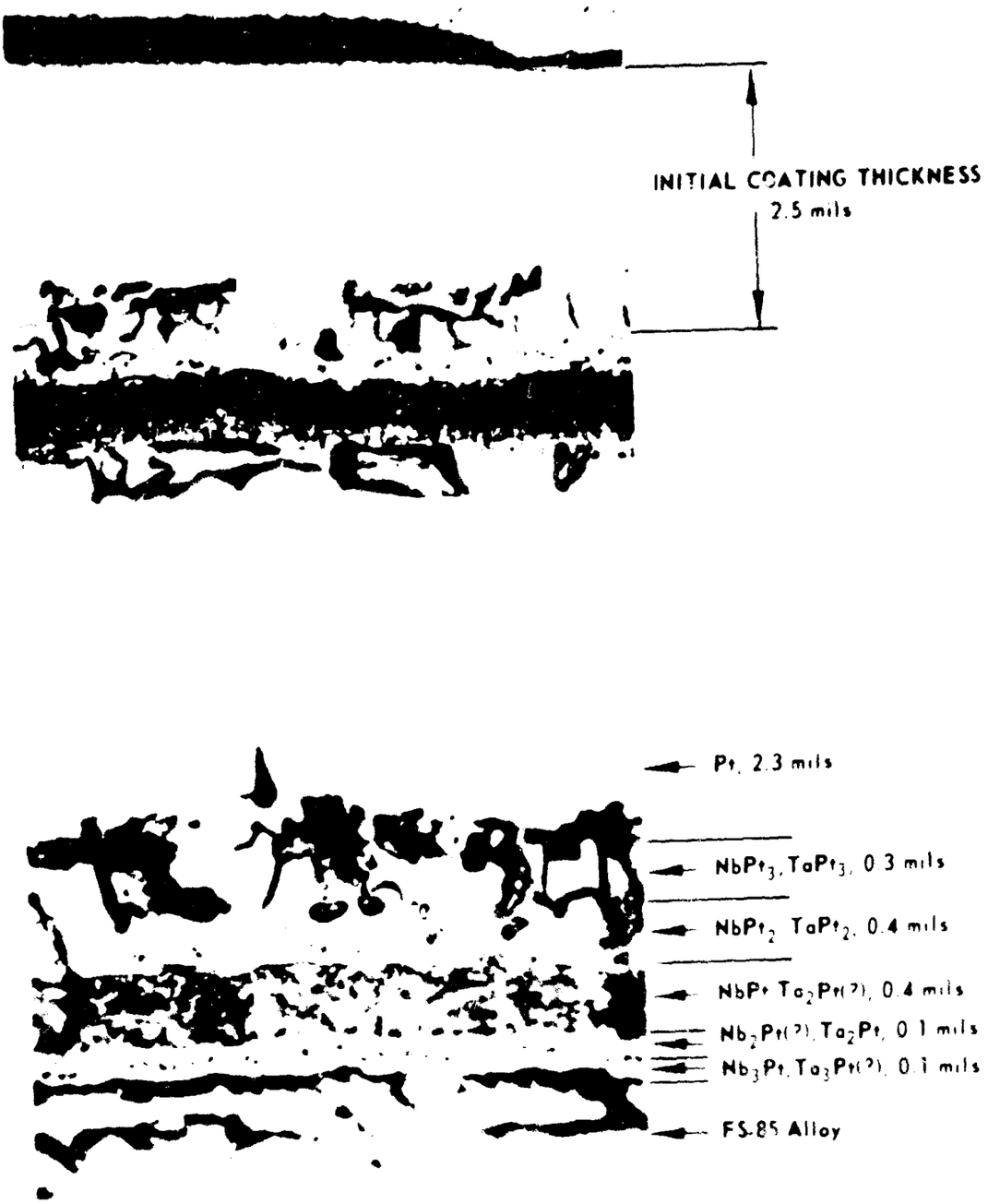
600X



1000X

FIGURE 62

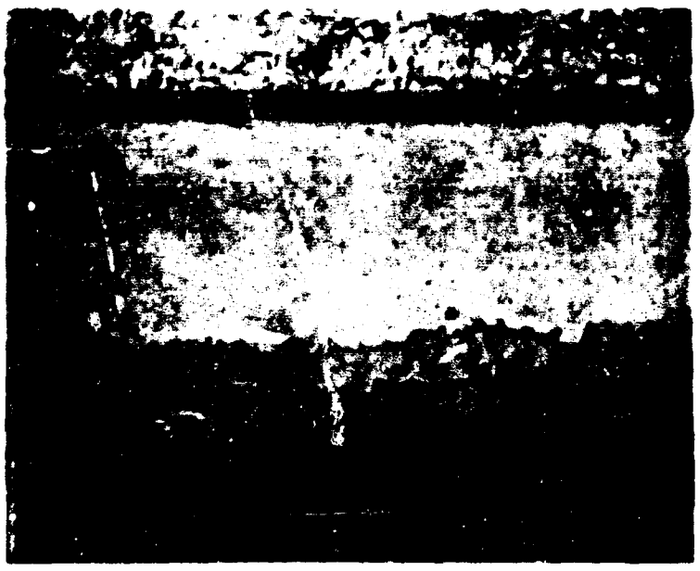
Polished and Etched Cross Section of a Platinum Clad FS-85 Sample After Heating 7 Hours at 2550 F in a 240 ipm Air Flow



1000X

FIGURE 63

Polished and Etched Cross Section of a Platinum Clad FS-85 Sample After Heating 7 Hours at 2550 F in a 240 ipm Nitrogen Flow



600X

1600X

FIGURE 64

Polished and Etched Cross Section of a Platinum-10% Rhodium Clad FS-85 Sample After Heating 6 Hours at 2550 F in a 240 ipm Air Flow

600X

1600X

FIGURE 65

Polished and Etched Cross Section of a Platinum 10% Rhodium Clad FS-85 Sample After Heating 6 Hours at 2550 F in a 240 ipm Nitrogen Flow

600X

1000X

FIGURE 66

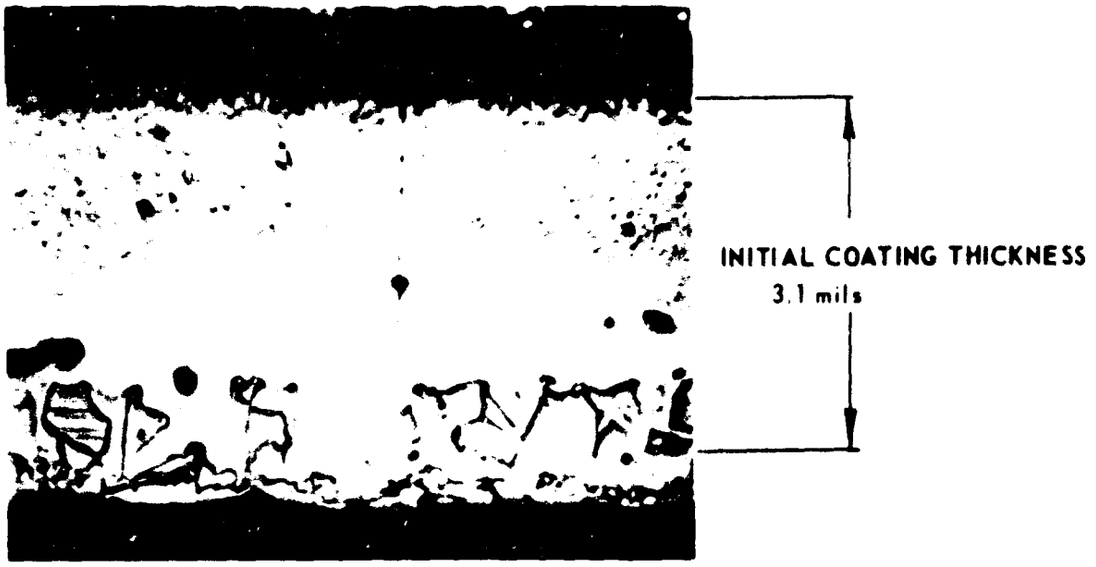
Polished and Etched Cross Section of a Platinum-2.5% Palladium Clad TZM Sample After Heating 14 Hours at 2550 F in a 240 ipm Air Flow

600X

1000X

FIGURE 67

Polished and Etched Cross Section of a Platinum-2.5% Palladium Clad TZM Sample After Heating 13 Hours at 2550 F in a 240 cpm Nitrogen Flow

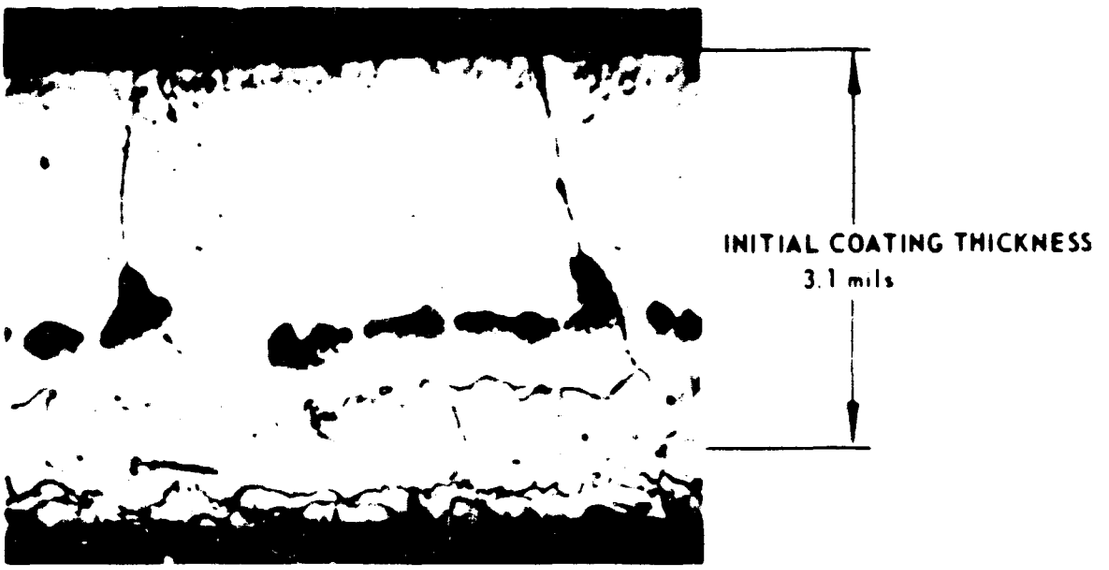


600X

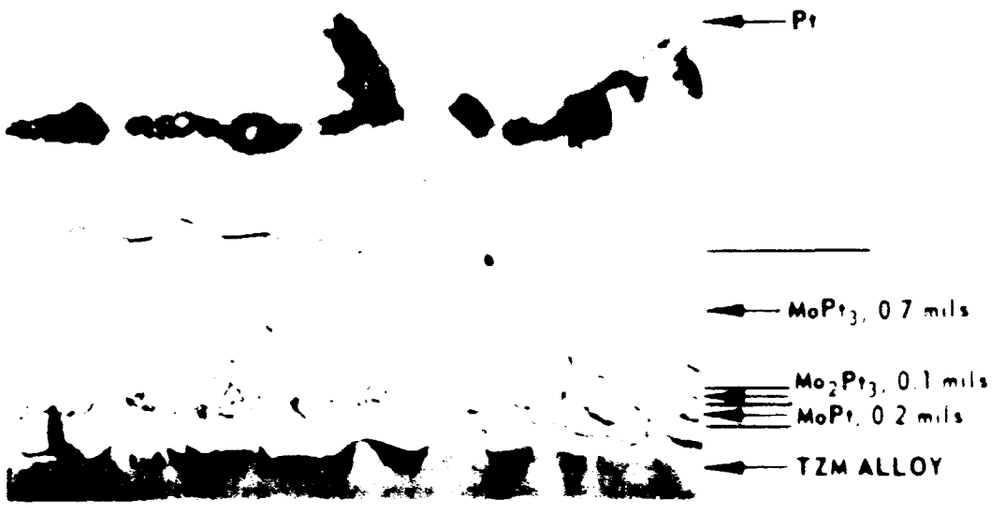
1600X

FIGURE 68

Polished and Etched Cross Section of a Platinum Clad TZM Sample After Heating 16 Hours at 2550 F in a 240 ipm Air Flow



600X



1000X

FIGURE 69

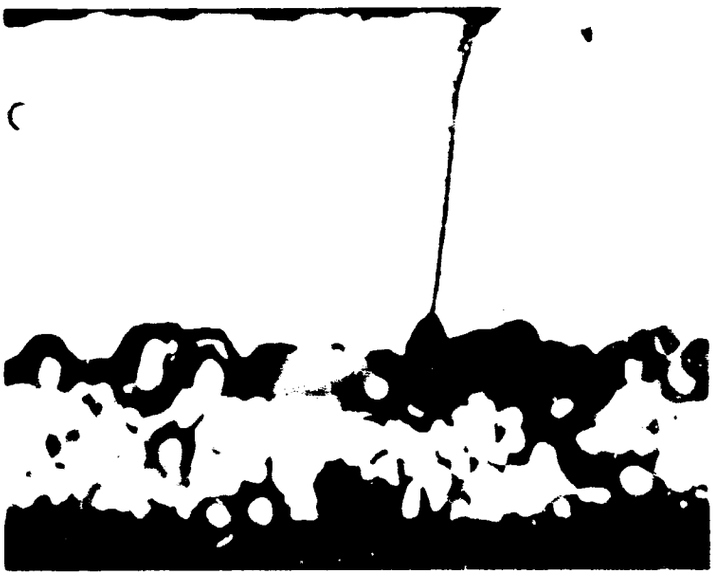
Polished and Etched Cross Section of a Platinum Clad TZM Sample After Heating 16 Hours at 2550 F in a 240 cpm Nitrogen Flow

1000X

1600X

FIGURE 70

Polished and Etched Cross Section of a Platinum-10% Rhodium Clad TZM Sample After Heating 5 Hours at 2550°F in a 240 lpm Air Flow



1000X

1600X

FIGURE 71

Polished and Etched Cross Section of a Platinum-10% Rhodium Clad TZM Sample After Heating 5 Hours at 2550 F in a 240 cm Nitrogen Flow

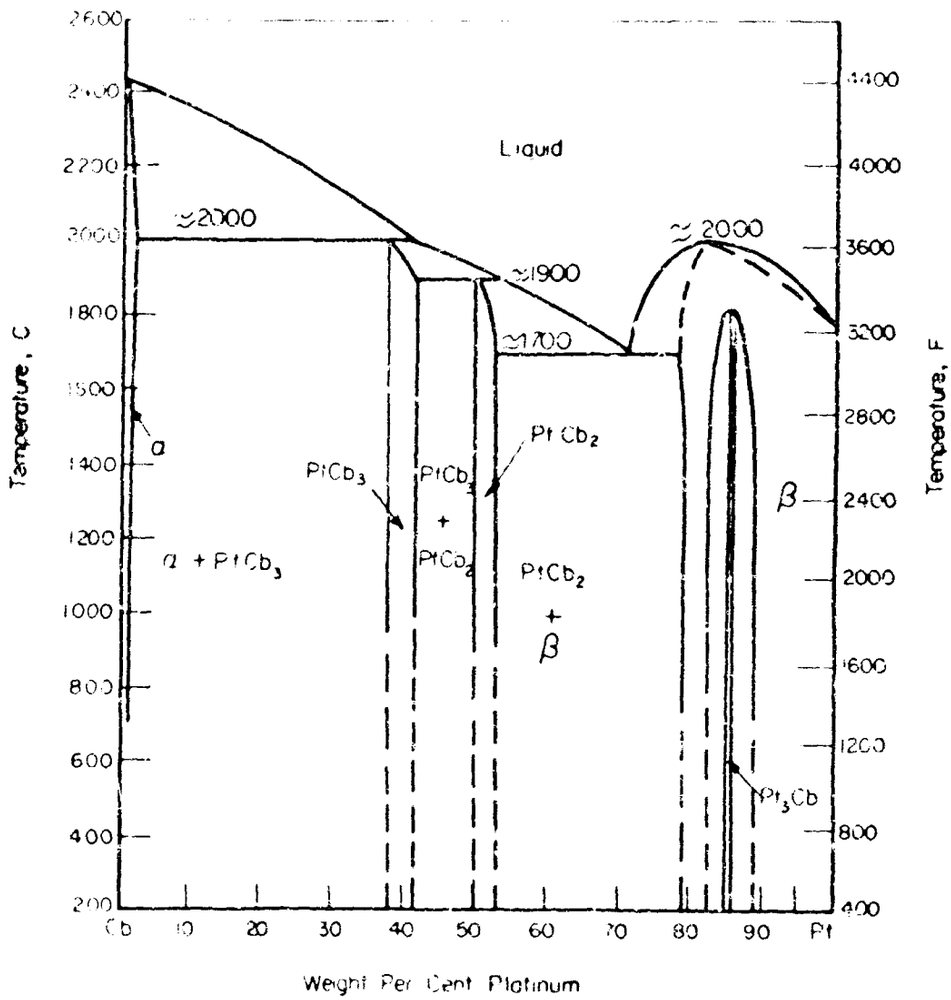


FIGURE 72 Platinum – Columbium Phase Diagram (Ref. 30).

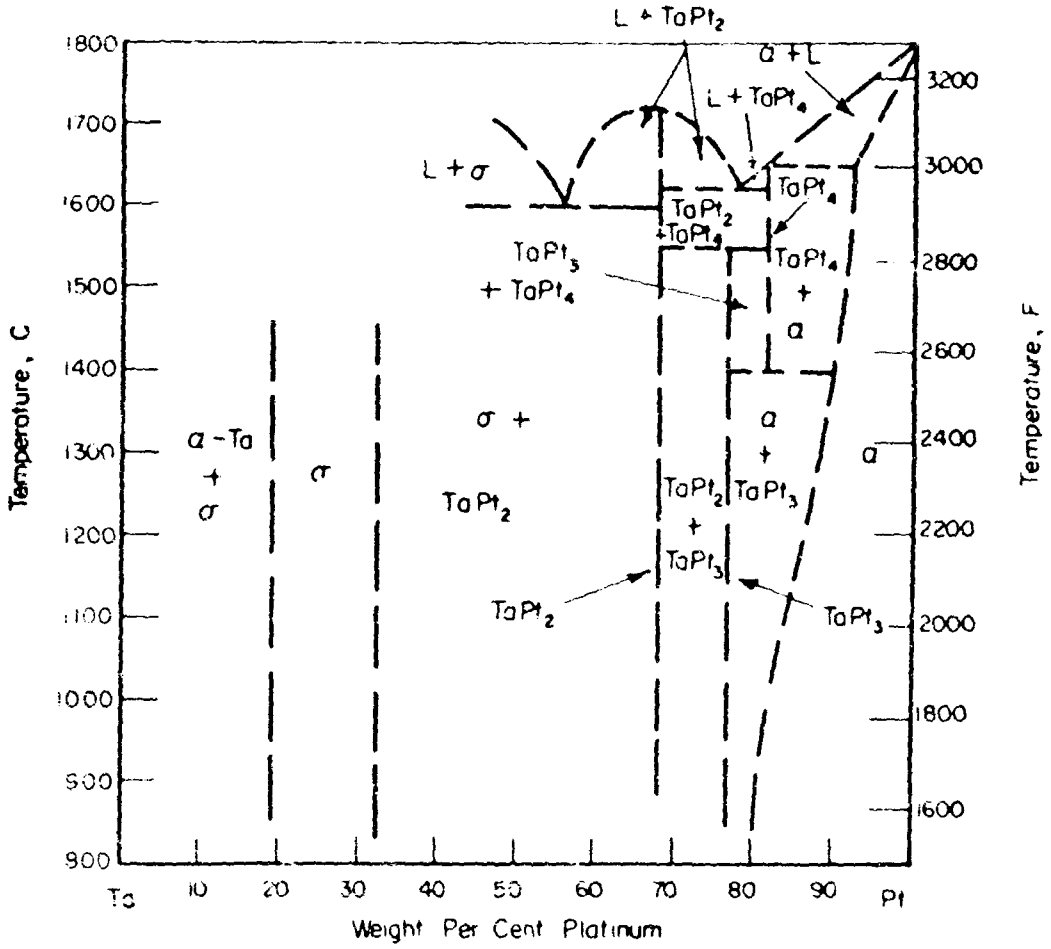


FIGURE 73 Platinum – Tantalum Phase Diagram (Ref. 31).

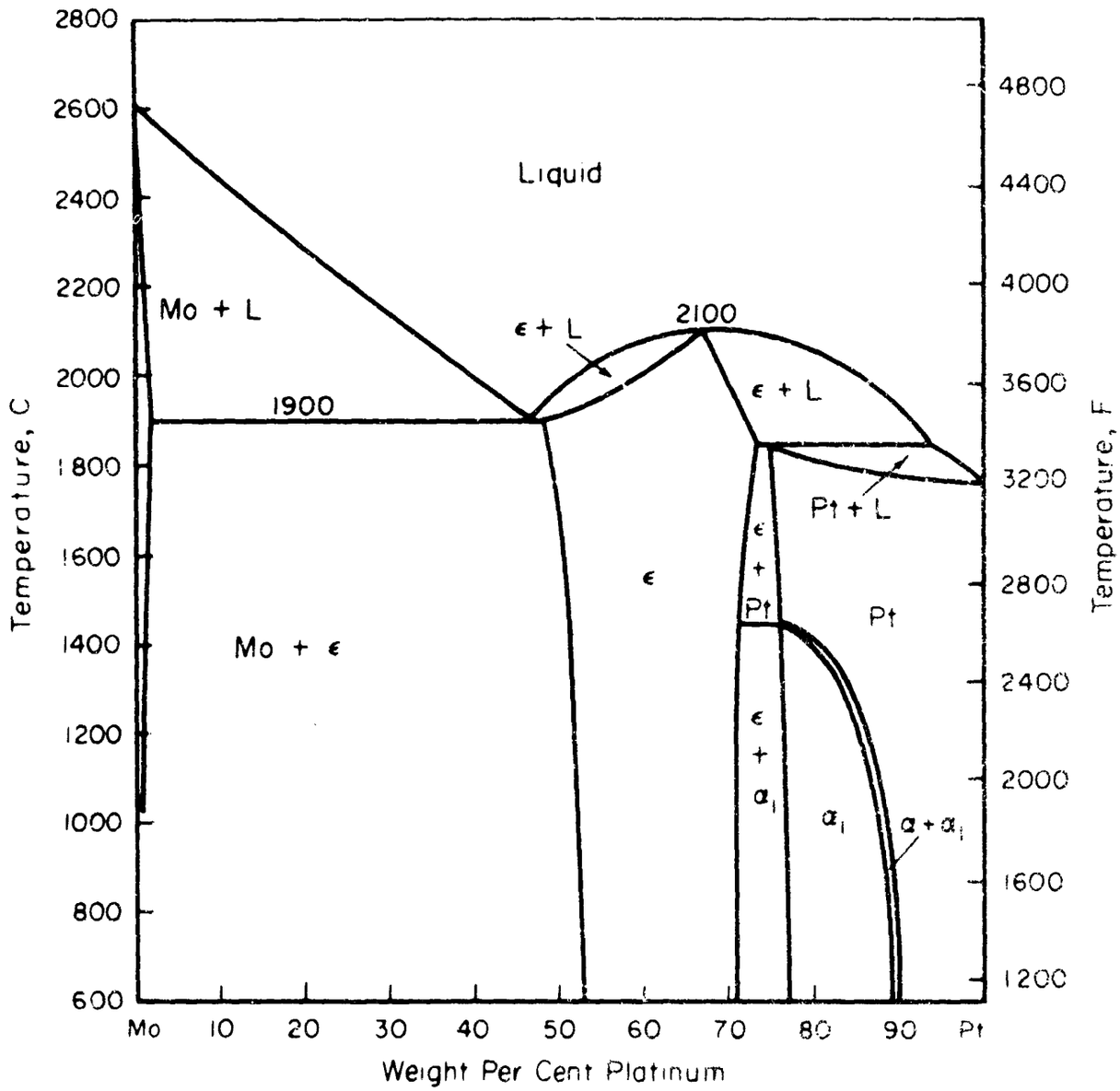


FIGURE 74 Platinum – Molybdenum Phase Diagram (Ref. 32).

100X

FIGURE 75

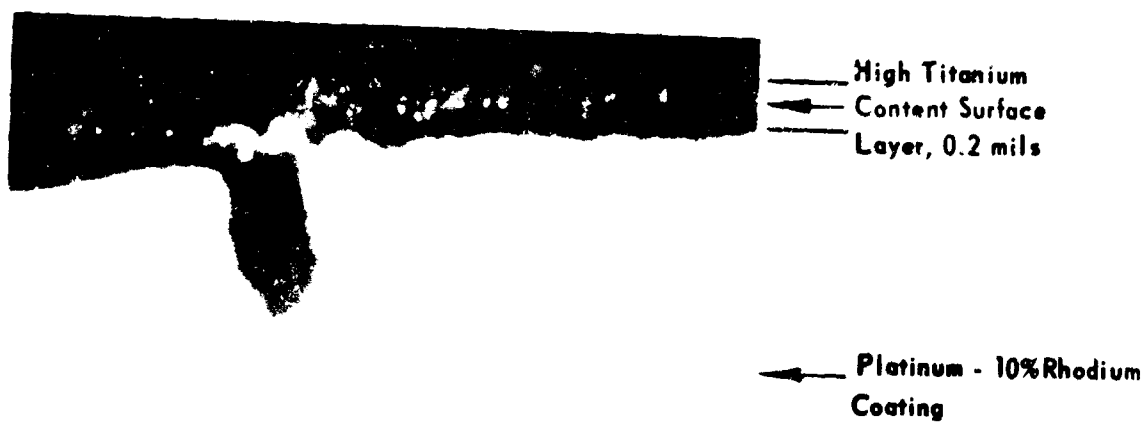
Polished and Etched Cross Section of a Platinum Clad FS-85 Sample Showing an Oxide "Blister" Formed after 7 Hours of Heating at 2550°F in a 240 ipm Air Flow

400X

400X

FIGURE 76

Polished and Etched Cross Section of a Platinum-10% Rhodium Clad TZM Sample Showing "Void" Areas in Early (Top) and Late (Bottom) Stages of Formation After Heating 5 Hours at 2550 F in a 240 ipm Air Flow



1600X

FIGURE 77

Polished and Etched Cross Section of a Platinum-10% Rhodium Clad TZM Sample with Focus on the Surface Layer after Heating 5 Hours at 2550°F in a 240 ipm Air Flow

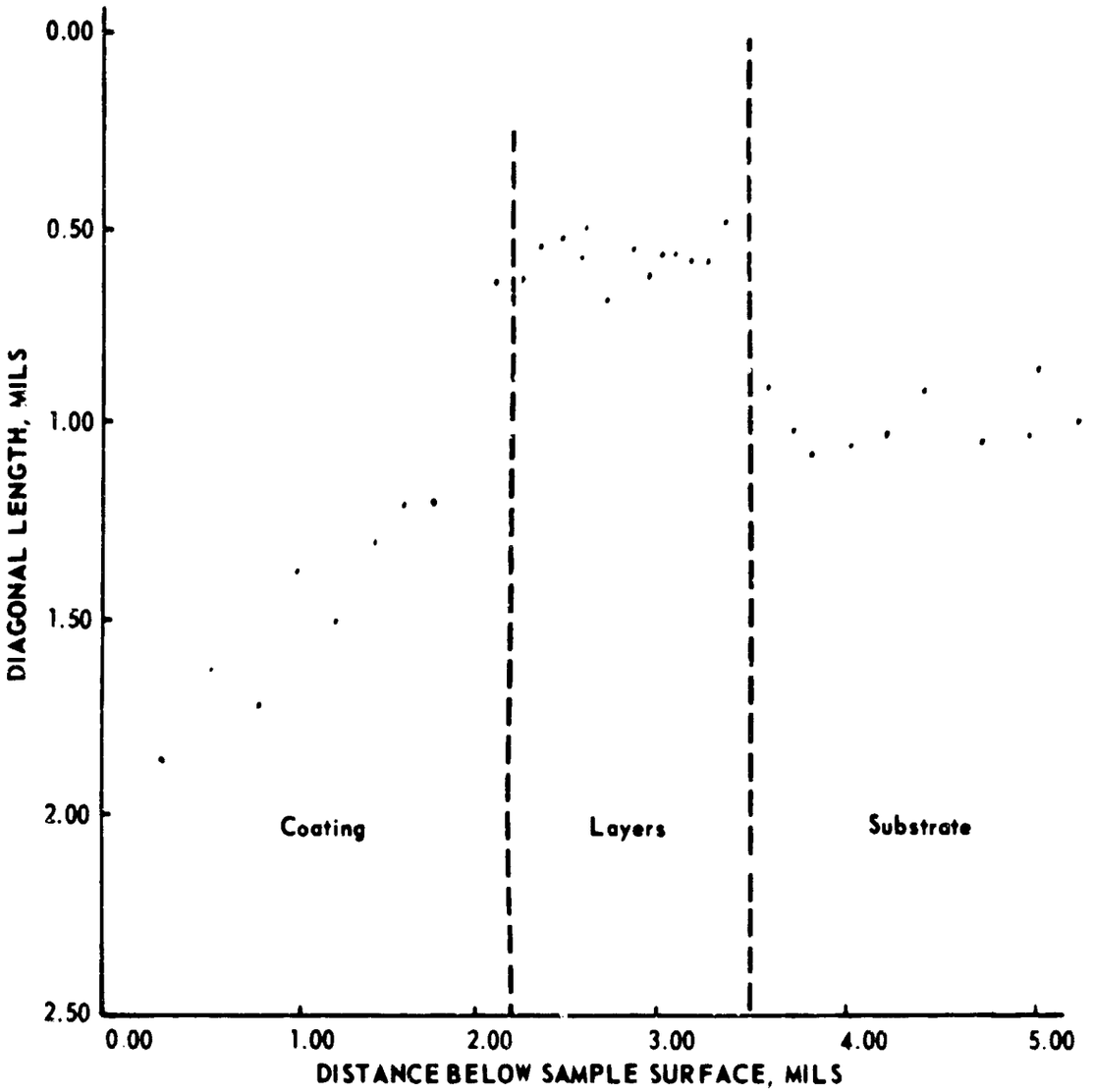


FIGURE 78 Microhardness Values Across the Cross Section of a Platinum Clad FS-85 Sample Tested 7 Hours at 2550°F in a 240 ipm Air Flow

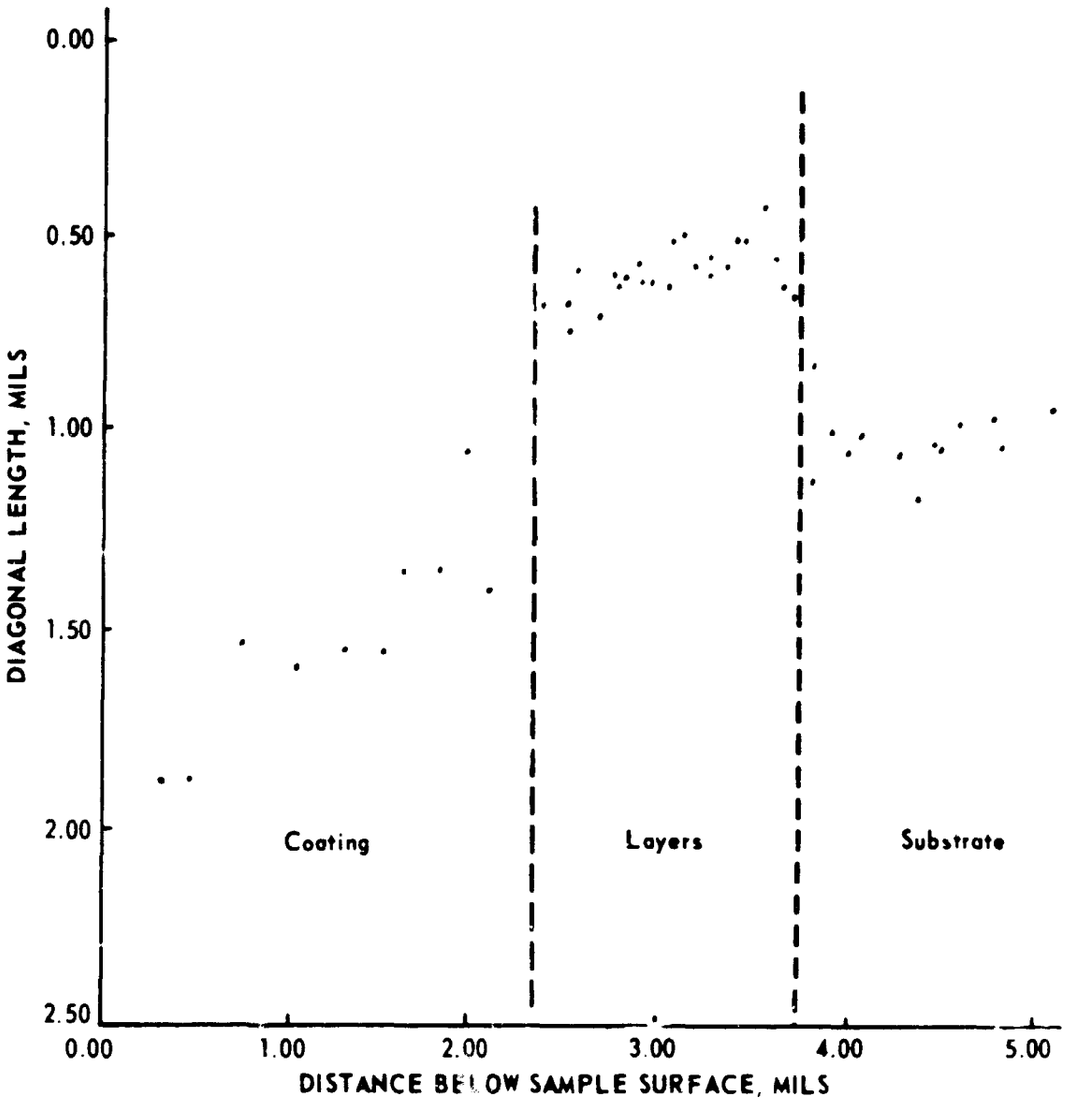


FIGURE 79 Microhardness Values Across the Cross Section of a Platinum Clad FS-85 Sample Tested 7 Hours at 2550° F in a 240 ipm Nitrogen Flow

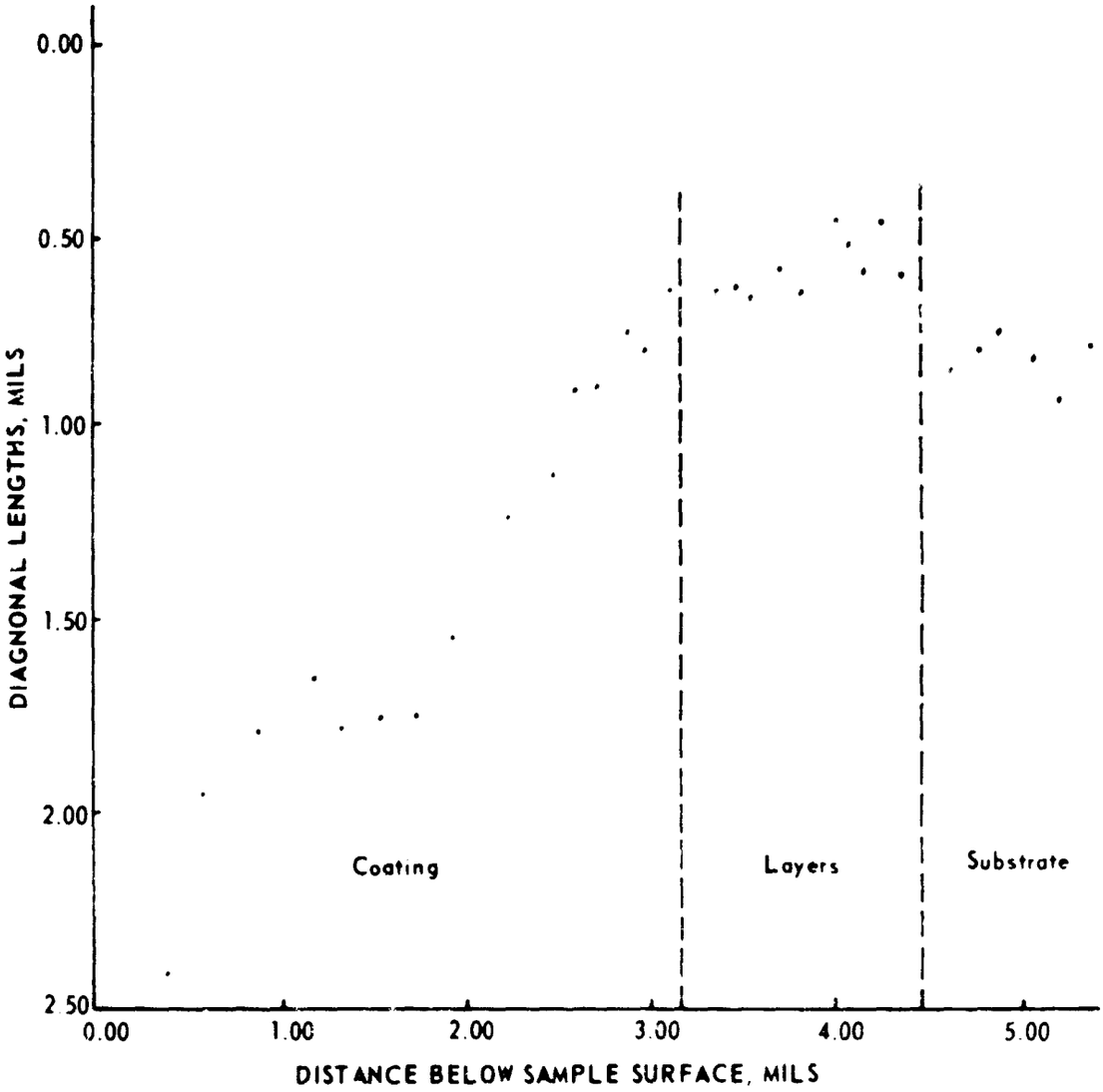


FIGURE 80 Microhardness Values Across the Cross Section of a Platinum Clad TZM Sample Tested 16 Hours at 2550 F in a 240 ipm Air Flow

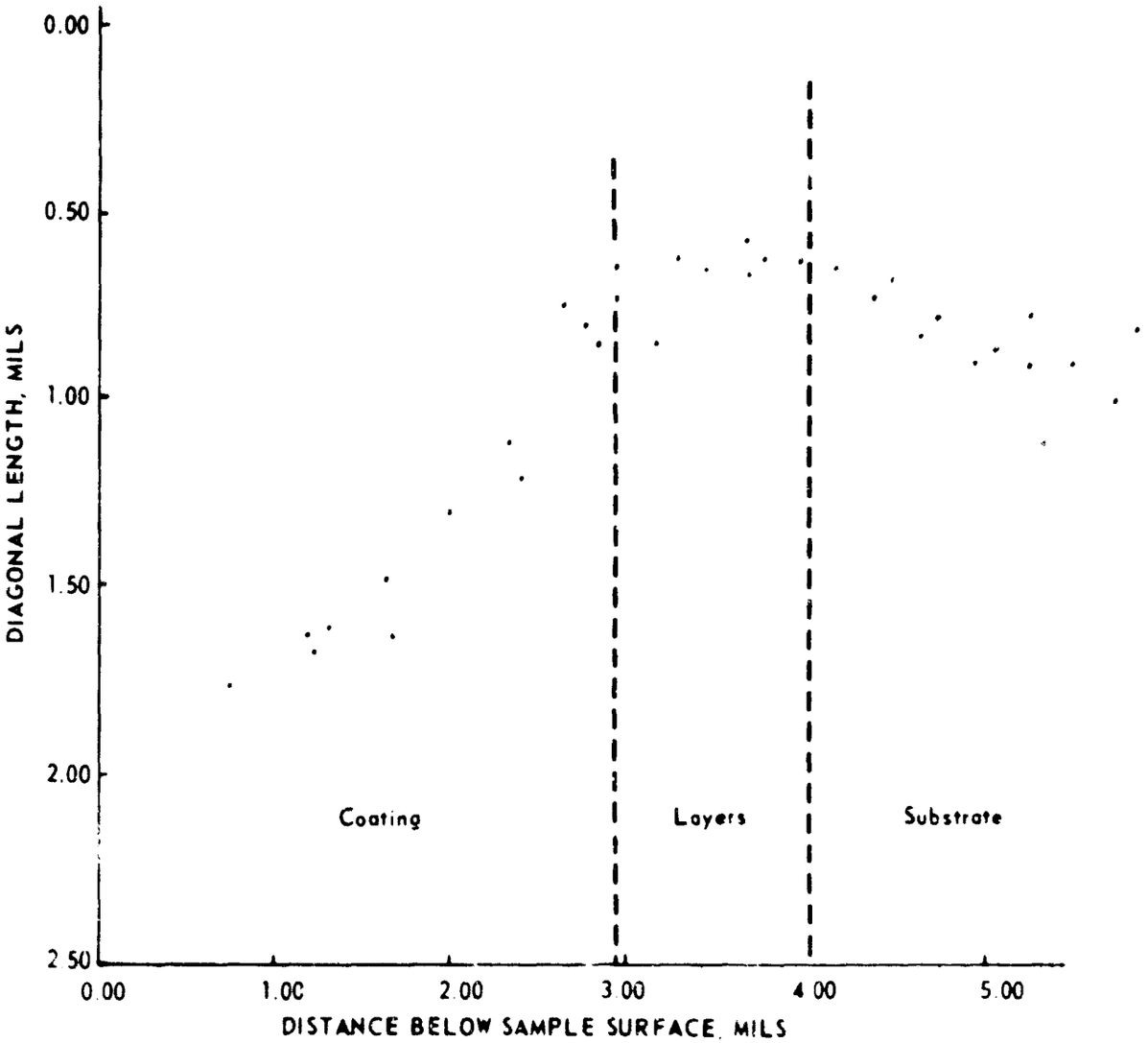


FIGURE 81 Microhardness Values Across the Cross Section of a Platinum Clad TZM Sample Tested 16 Hours at 2550 F in a 240 cpm Nitrogen Flow

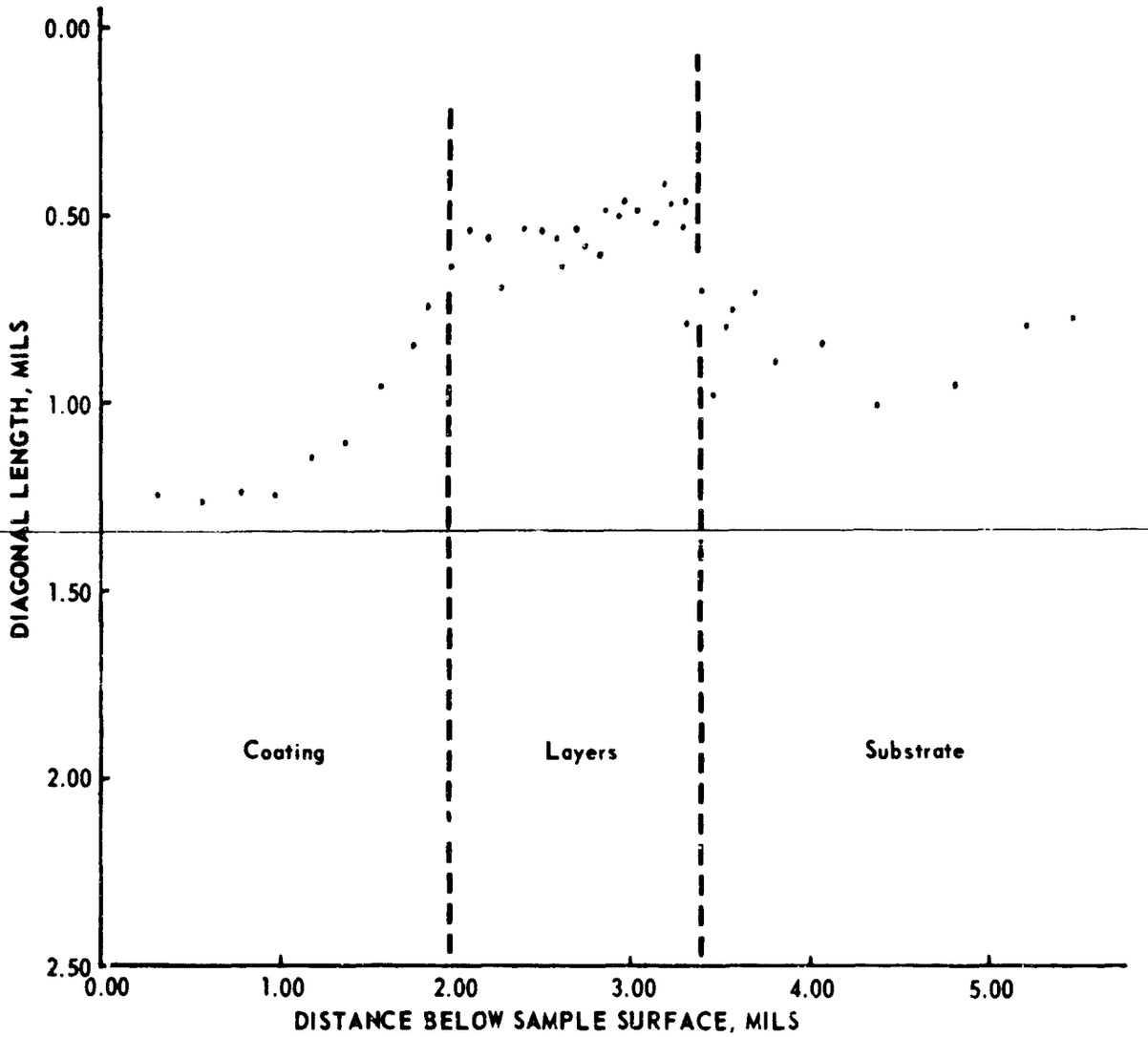


FIGURE 82 Microhardness Values Across the Cross Section of a Platinum-10% Rhodium Clad FS-85 Sample Tested 6 Hours at 2550°F in a 240 ipm Air Flow

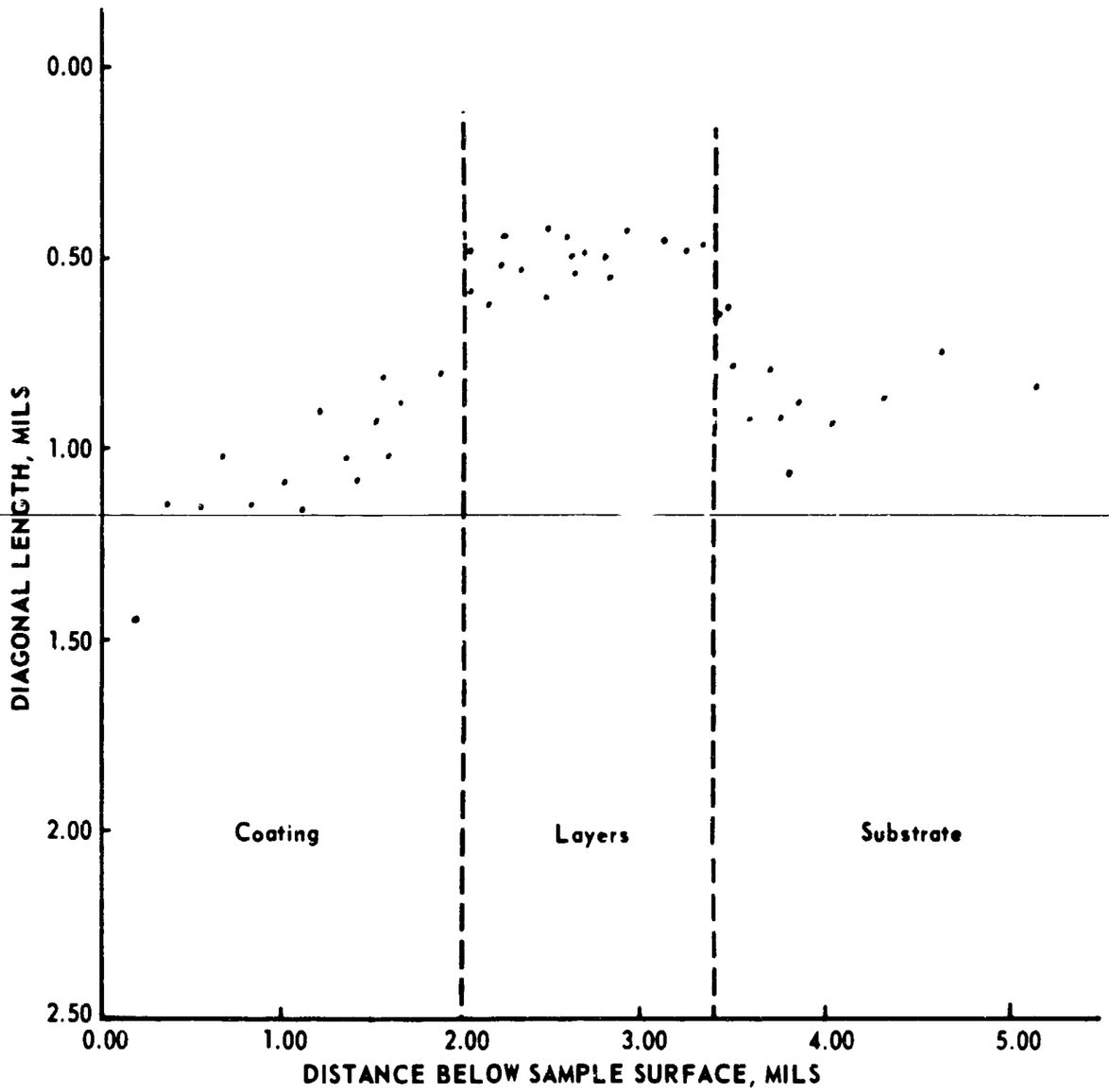


FIGURE 83 Mircohardness Values Across the Cross Section of a Platinum-10% Rhodium Clad FS-85 Sample Tested 6 Hours at 2550°F in a 240 ipm Nitrogen Flow

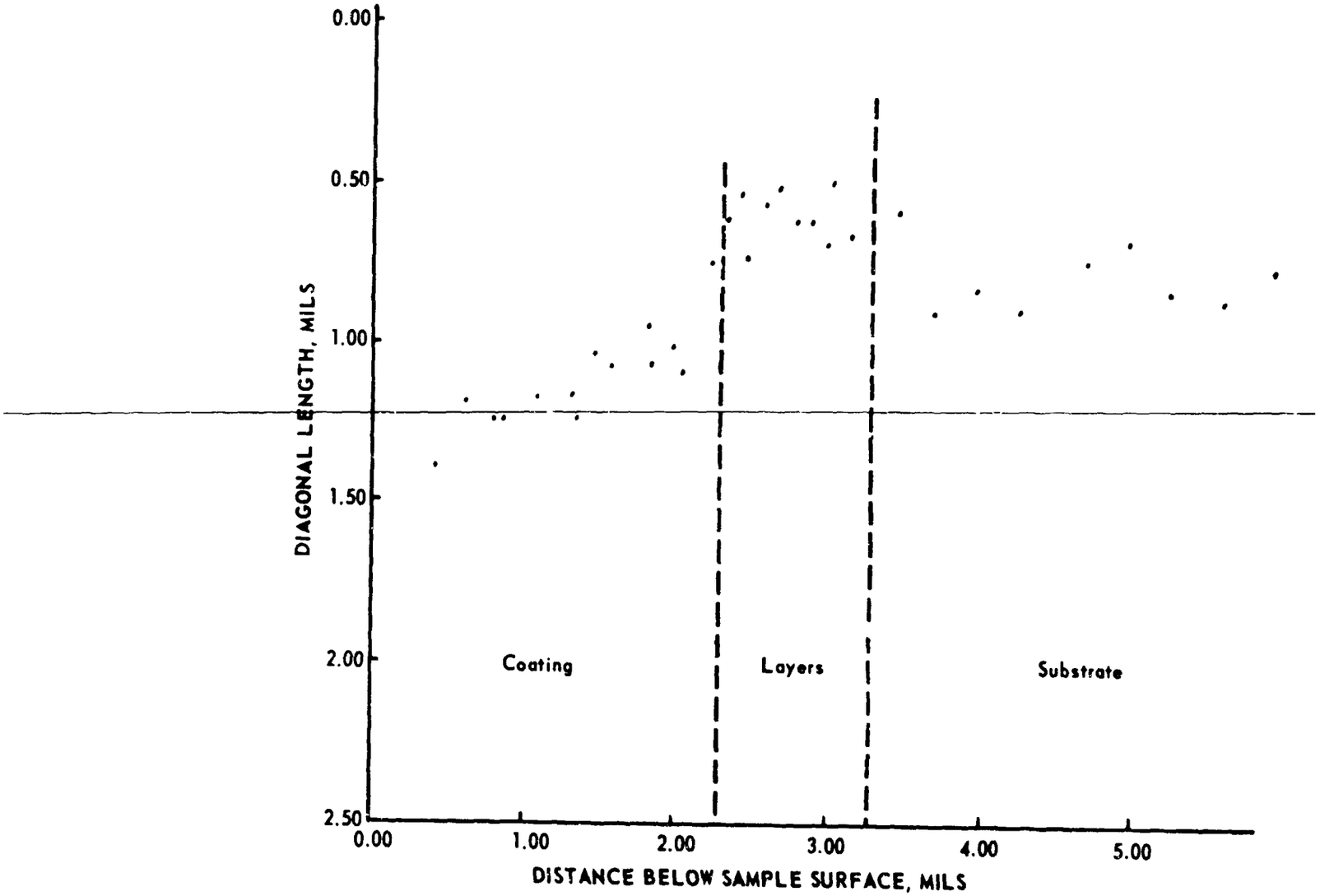


FIGURE 84 Microhardness Values Across the Cross Section of a Platinum-10% Rhodium Clad TZM Sample Tested 7 Hours at 2550°F in a 240 ipm Air Flow

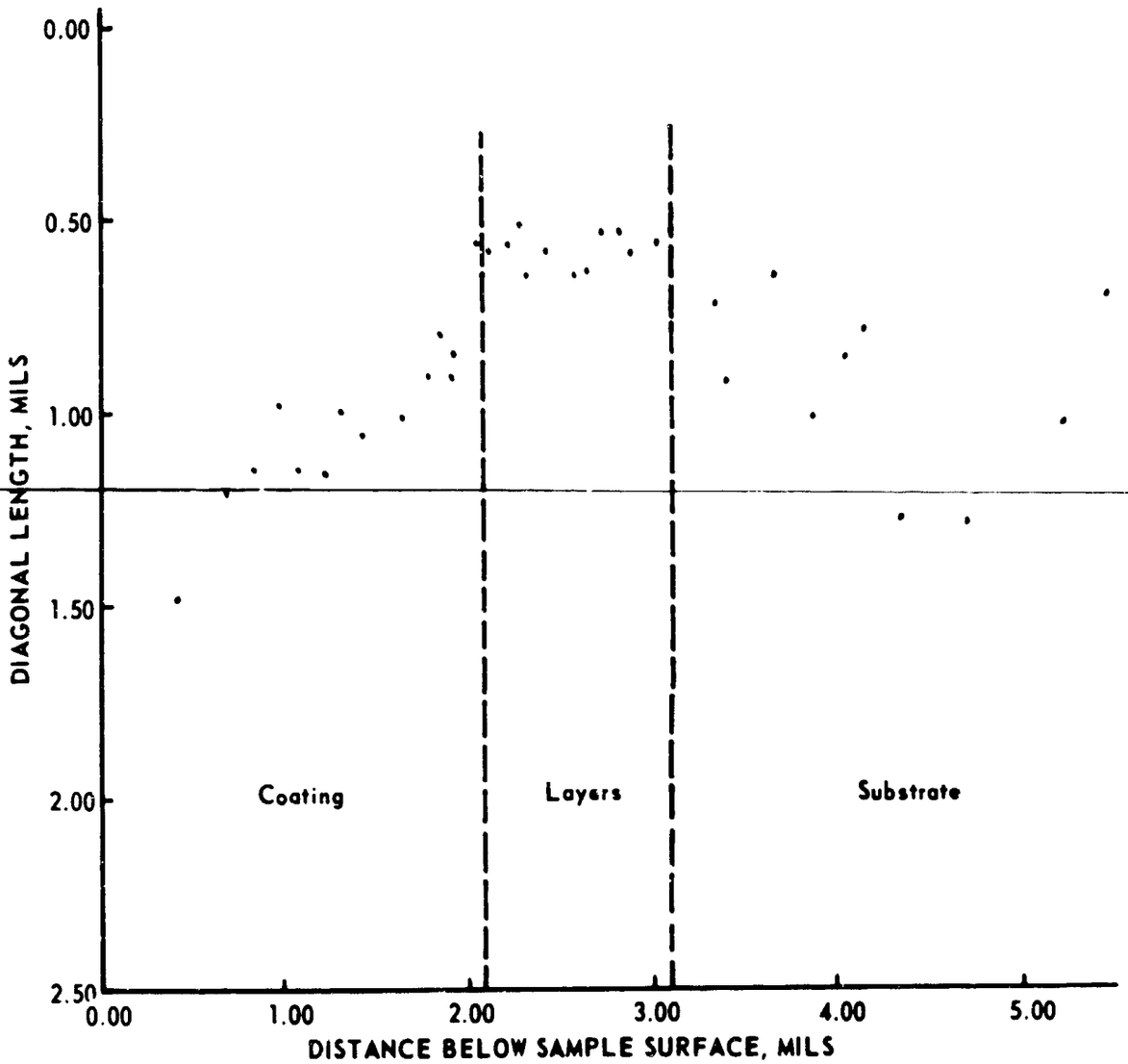


FIGURE 85 Microhardness Values Across the Cross Section of a Platinum-10% Rhodium Clad TZM Sample Tested 7 Hours at 2550°F in a 240 ipm Nitrogen Flow

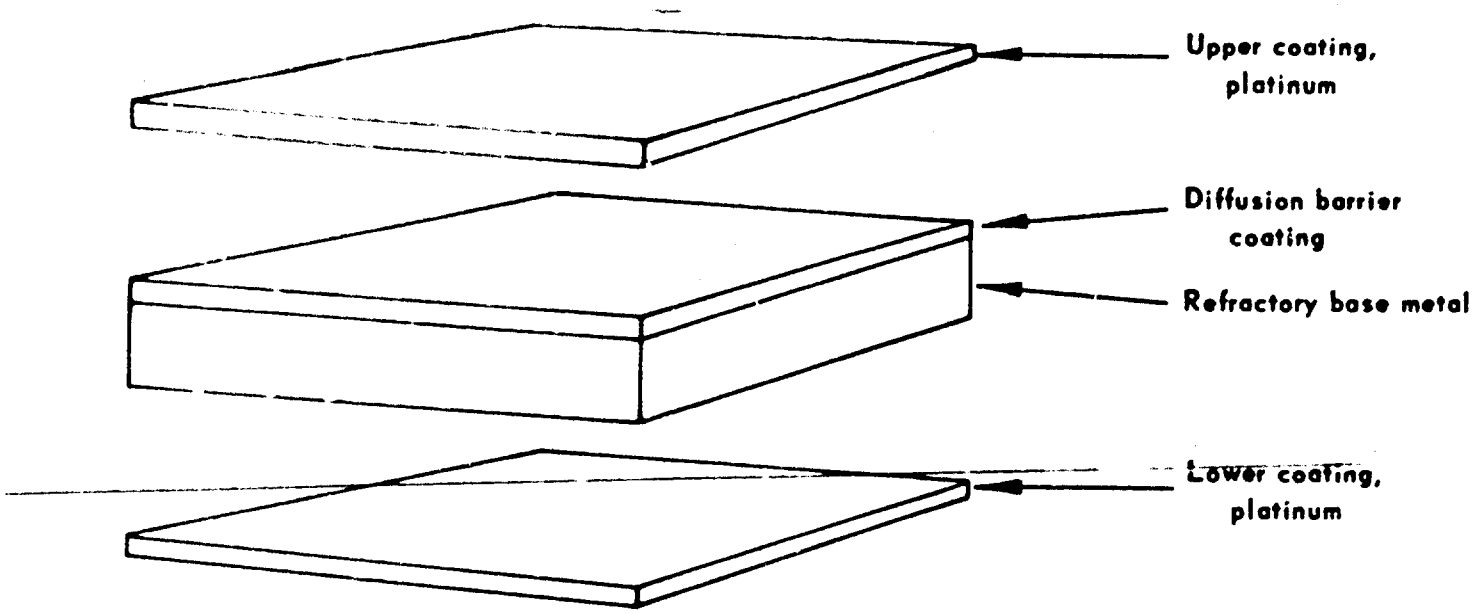


FIGURE 86 Diffusion Barrier Test Sample

ıg,

rrier

ɔsc metal

g,

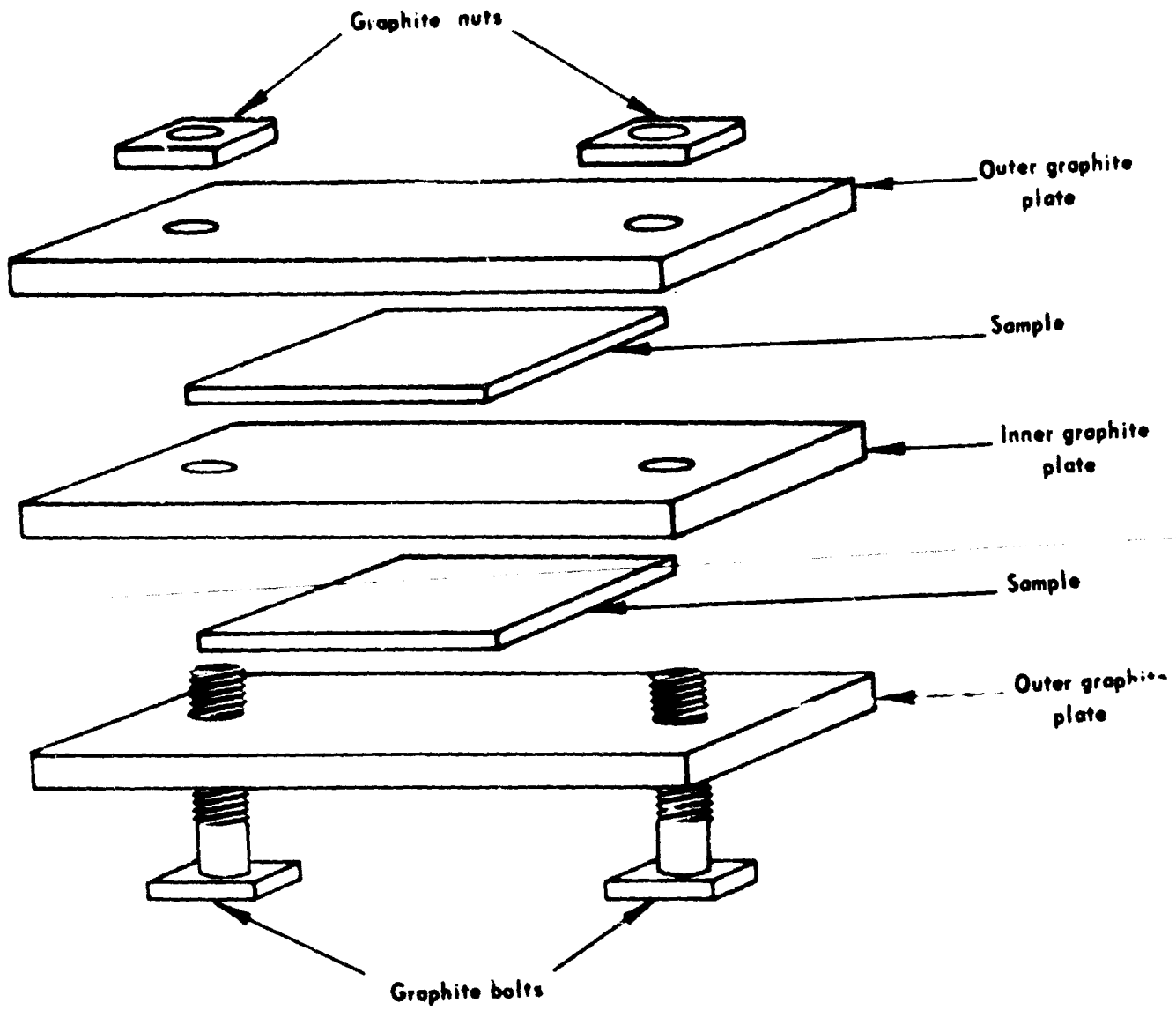
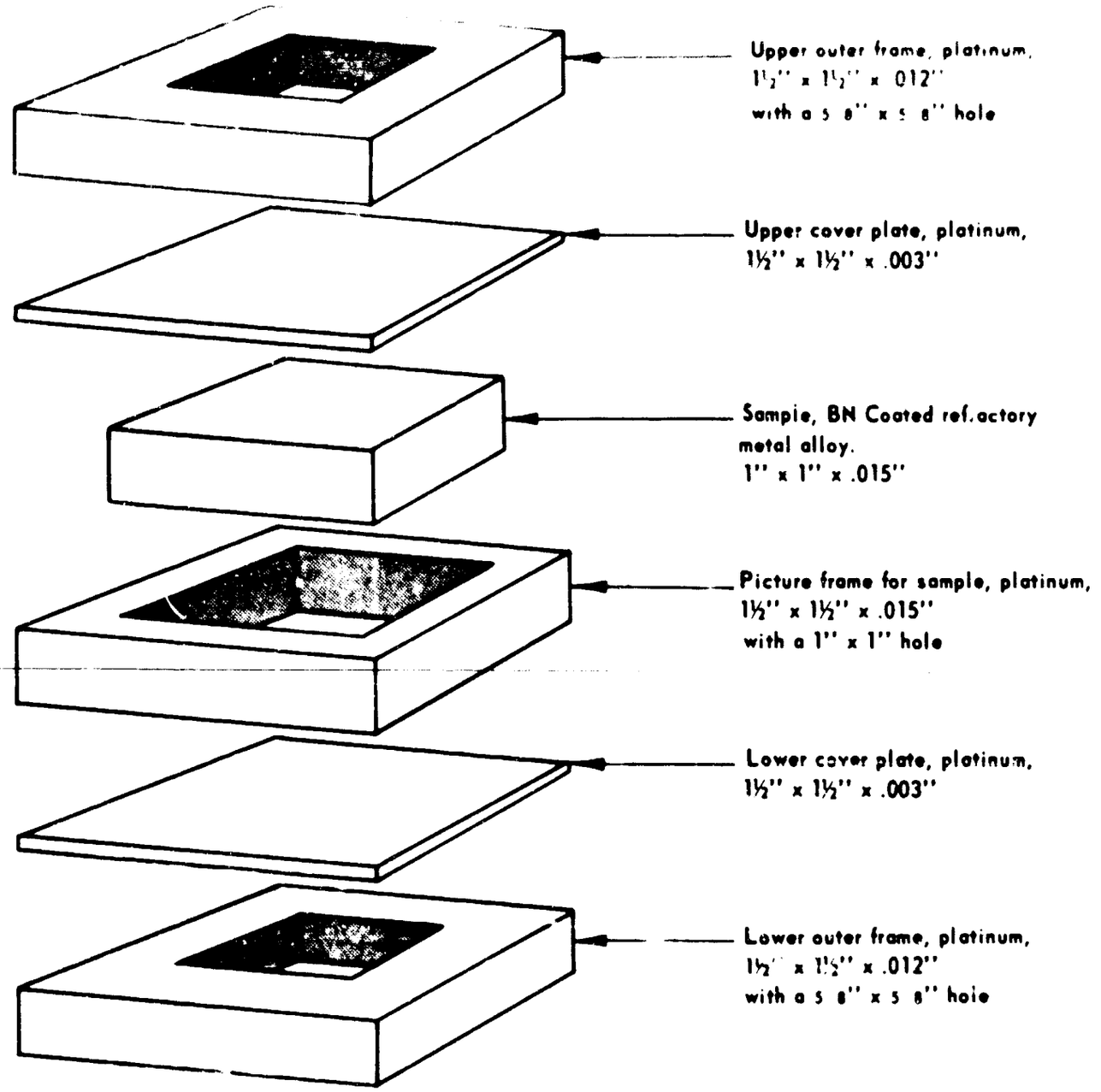


FIGURE 87 Graphite Clamp for Testing Diffusion Barriers

50X

FIGURE 88 Cross Section of a Hot Roll Bonded Composite Consisting of a Platinum-10% Rhodium Coating, a Rhenium Intermediate Layer (Broken Up), and an FS-85 Substrate



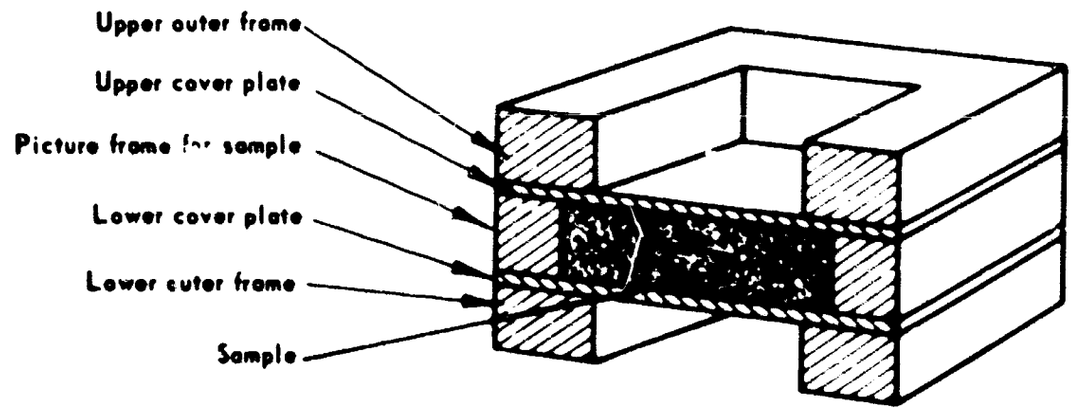


FIGURE 89

Special picture frame setup for testing
Boron Nitride coated refractory metal alloys.

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